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ENVIRONMENTAL IMPACT OF HEAVY METAL POLLUTION IN NATURAL AQUATIC SYSTEMS

by

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'In the Name of Allah, Most Gracious, Most Merciful'

"Read! and thy Lord is Most Bountiful,

He who taught the use of the pen,

Taught man that which he knew not"

Al Quran, Sura XCVI 3-5

ABSTRACT

The distribution of heavy metals between soil and soil solutions is a key issue in evaluating the environmental impact of long term applications of heavy metals to land. Contamination of soils by heavy metals has been reported by many workers. Metal adsorption is affected by many factors, including soil pH, clay mineralogy, abundance of oxides and organic matter, soil composition and solution ionic strength. The pH is one of the many factors affecting mobility of heavy metals in soils and it is likely to be the most easily managed and the most significant. To provide the appropriate level of protection for aquatic life and other uses of the resource, it is important to be able to predict the environmental distribution of important metals on spatial and temporal scales and to do so with particular emphasis on the water column concentrations. Regulatory levels reflected in water quality criteria or standards are based on water column concentrations. Predicting water column concentrations requires a consideration of the interactions of water column contaminants with both bed sediments and suspended particulates as critical components in the assessment.

The adsorption behaviour of cadmium, copper, lead and zinc onto soils is studied under the various geo-environmental conditions of pH, concentration of adsorbate and adsorbent, and solution compositions. Experiments were conducted to determine the equilibrium contact time of various adsorbates for adsorbent in different systems. Experiments were also conducted to check the efficiency of various acid-mixtures to extract heavy metal from soils into the aqueous phase. The adsorption behaviour of heavy metals onto soils was also studied from sea-water system.

Soils are characterized in terms of the role of clay minerals to remove the metals from the solution phase, back-ground levels of metals, maximum adsorption capacity to adsorb various heavy metals from different adsorption systems, and type of surface sites present. The experimental data of metal adsorption is described by Langmuir adsorption model. The adsorption data are also expressed in terms of surface loading, surface acidity, adsorption density, and affinity of soils for heavy metals in different adsorption systems. Ecological implications of changes in physical and chemical conditions in aquatic systems on heavy metals uptake by soils are also discussed.

This research covers the following areas:
the environmental impact of heavy metal discharge into the aquatic systems, the study of the mobility patterns of different heavy metals as function of geo-environmental conditions, and determination of the pathways and the ultimate fate of heavy metals in the environment.

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1.0 INTRODUCTION

The transport of metals to groundwater from hazardous waste sites is of considerable environmental concern. Assessments completed by EPA in the 1970 's (Scalf et al., 1973; Miller et al., 1974; and Pye and Patrick, 1983) suggest four pollutants most commonly found in groundwater: chlorides, nitrates, hydrocarbons and heavy metals. Soon after the Minamata disease discovered in Japan several other heavy metals have been found to accumulate up food chains and to be toxic to aquatic and terrestrial life often at very low concentrations. Largely in response to potential health hazards, much research has been directed toward understanding reactions of metals in the natural environment. One of the most important aspects of the research has been an attempt to determine pathways and the ultimate fate of heavy metals in the environment.

Man's activities have disturbed the natural distribution of heavy metals in the environment on land and in rivers, lakes and seas. Trace metals exist in different forms in the sediment-water system. Some of metals may stay in water as free or complexed ions or adsorbed onto solids, some may incorporate within insoluble organic or inorganic matter. Considering the extremely low levels of metals found in present-day oceans, despite the continuous inputs from land sources, it would seem that the sediments are the permanent sink of soluble trace metals. The inability of water to extract metals from sediments may explain why metal concentrations in natural waters are so low. Heavy metals entering a water system are rapidly removed from solution by interaction with the components of sediments such as clay minerals, hydrous metal oxides and organic matter. When evaluating the environmental impact of the discharge of heavy metals into an aquatic system it is important to determine the extent and rate at which foreign metal species equilibrate with the natural pool of dissolved metal species in water and underlying sediments. Various mechanisms for metal mobilization have been proposed. These include desorption (Rohatgi & Chen,1975), dissolution (Brook & Presley,1968), redox reactions (Stumm & Morgan,1970), complex formation (Linberg,1974) and physical disturbance (Wakeman,1974).

One of the most important processes controlling the transport of heavy metals is adsorption onto solid surfaces. In natural aquatic systems metals are partitioned between the dissolved and particulate phases, probably only the fraction associated with the solid surface (adsorbed) is easily exchangeable with the aqueous phase. It has been suggested that adsorptive interactions with clays and oxide surfaces may exert the major control on dissolved metal concentrations in marine, fresh water and soil environments (Jenne,1968).

The need for better understanding of trace metal adsorption has wider importance than answering the question of whether river-borne detritus is a source or sink of heavy metals. It is necessary to know the changing conditions that will effect trace metal adsorption in order to intelligently manage enterprises such as the dumping of dredge spoils into an environment different from the designing site or controlling effluent from industrial sources. The environmental impact of heavy metals is related to whether metals are dissolved and therefore transported with a water mass or adsorbed and hence capable of settling out of solution in localized areas. Just which form is less hazardous, or whether it is hazardous at all, depends on the location. If the metals are adsorbed and the sediment lies in an environmentally isolated area it could seem beneficial to enhance adsorption. If the sediments are a source of heavy metals into benthic organisms and into a food chain it would seem beneficial to solubilize the metals. The best approach depends on a given situation since one must consider the total amount of metal involved, its input rate, its site and the mixing characteristics of the receiving water mass, the geo-chemical interactions in the area and the biological effects of heavy metals.

Transport of metals to groundwater from hazardous waste sites is of considerable environmental concern. Pye & Patrick (1983) suggest four pollutants most commonly found in groundwater: chlorides, nitrates, heavy metals and hydrocarbons. Many contaminants have been found in higher concentrations in groundwater rather than in surface water (Page,1981). Metal ion levels in natural water ways can be significantly influenced by interactions involving other components such as clay particles and dissolved organic matter (Slavek & Pickering,1981). Studies have identified heavy metals contamination in sediments (Eduljee et al.,1985) and in waters (Paulson & Feely,1985; Laumond et al.,1984).

Chemicals used in medicine, in the home, in agriculture and in industry have done much to better health, increase food production and raise living standards. They have also brought new dangers, for they find their way into the environment by different paths, both intentionally and unintentionally, and can enter food and water supplies. The presence of heavy metals in natural waters has become a significant topic of concern for environmentalists, scientists and engineers in various fields associated with water quality and growing awareness of the public. Direct toxicity to human and aquatic life and indirect toxicity through accumulation of metals in the aquatic food chain are the focus of this threatening concern. Elements such as cadmium exhibit human toxicity at extremely low concentrations and chromium, lead, copper and zinc are toxic at slightly higher concentrations (Peters et al.,(1978).

There are two ways to study any natural process. One is to collect natural samples and try to correlate several system parameters with one another. The second is to study model systems in controlled laboratory experiments. Clearly, the trade-off between the two involves applicability to natural systems in the first case versus ease of interpretation and greater potential for basic scientific advances in the second. For this study the latter approach was chosen.

It is hoped that the results partially link the gap between colloidal chemists, who are primarily interested in the physical and chemical properties of the interface, and geochemists and engineers interested in modelling behaviour in complex natural systems or in designing processes to remove heavy metals from water streams.

The metal adsorbates chosen were cadmium, copper, lead & zinc for intensive study and chromium, cobalt & nickel for comparative purposes. The specific goals of the study were:

1. To determine the effects of widely varying adsorbate and adsorbent concentrations on the adsorption behaviour of heavy metals onto soils.
2. To determine the effects of solution composition on the adsorption behaviour of these metals.
3. To explain the reactions to determine the pathways and the ultimate fate of these metals into the aquatic environment.

2.0 SOURCES OF HEAVY METALS IN THE AQUATIC ENVIRONMENT

2.1 Introduction

Heavy metals are natural constituents of every compartment of the environment. They take part in bio-geochemical reactions and are transported between compartments by natural processes, the rate of which are at times greatly altered by human activities. Cadmium, copper, lead and zinc are all chalcophilic and are often found in close association, particularly in sulphidic ore deposits.

Metals can be mobilized by natural weathering processes such as erosion or dissolution, or as a direct result or side effect of human activities. For example, acid mine drainage leaches metals from rocks and soils, oxides of cadmium and zinc are vaporized and released to the air during smelting (Fleischer et al.,1974), and lead is emitted from automobile exhaust pipes at an annual rate twice that of its worldwide mobilization by natural processes (Brook et al., 1968). Cadmium and lead are particularly noxious pollutants since many of their uses tend to disperse them widely in the environment making recycling very difficult. It is estimated that 10^6 kg of Cd and $3x10^9$ kg of Pb are released to the air annually (Brook et al., 1968). Much of this finds its way into water systems by direct fallout or via runoff streams. In addition to atmospheric fallout significant quantities of heavy metals are introduced to natural waters in domestic and industrial waste streams and in agricultural runoff, particularly in areas where phosphate fertilizer has been applied (Lee and Keeny,1975).

Once in the natural aquatic system metals can undergo a variety of transformations including in dissolved speciation, precipitation and oxidation/ reduction (Fig.1). All of these processes can drastically alter the mobility of the metals. The total concentration of dissolved metal species in water can be orders of magnitude greater than the concentration of free aquo metal due to the formation of soluble complexes with organic and inorganic ligands. The strength of complexes are affected by the identity of the atom involved and stereochemical factors.

In natural water systems the most important inorganic ligands are hydroxide, carbonate, sulphide and chloride (Leckie and James,1974). Bilinski et al.(1976) reported that carbonate complexes are the dominant inorganic forms of Pb and Cu in fresh water but Cd and Zn are not complexed. In oxygenated seawater the chloro-complexes of Cd, hydroxy complexes of Zn and Cu and carbonate complexes of Pb are the predominant inorganic species (Stumm & Brauner,1975). The bisulphide and polysulphide complexes dominate speciation of these four metals in sulphidic marine waters (Gardner,1974).

Dissolved organic ligands tend to be present at much lower concentrations and tend to bind some more metals much more strongly than inorganic ligands. While there have been some attempts to identify specific

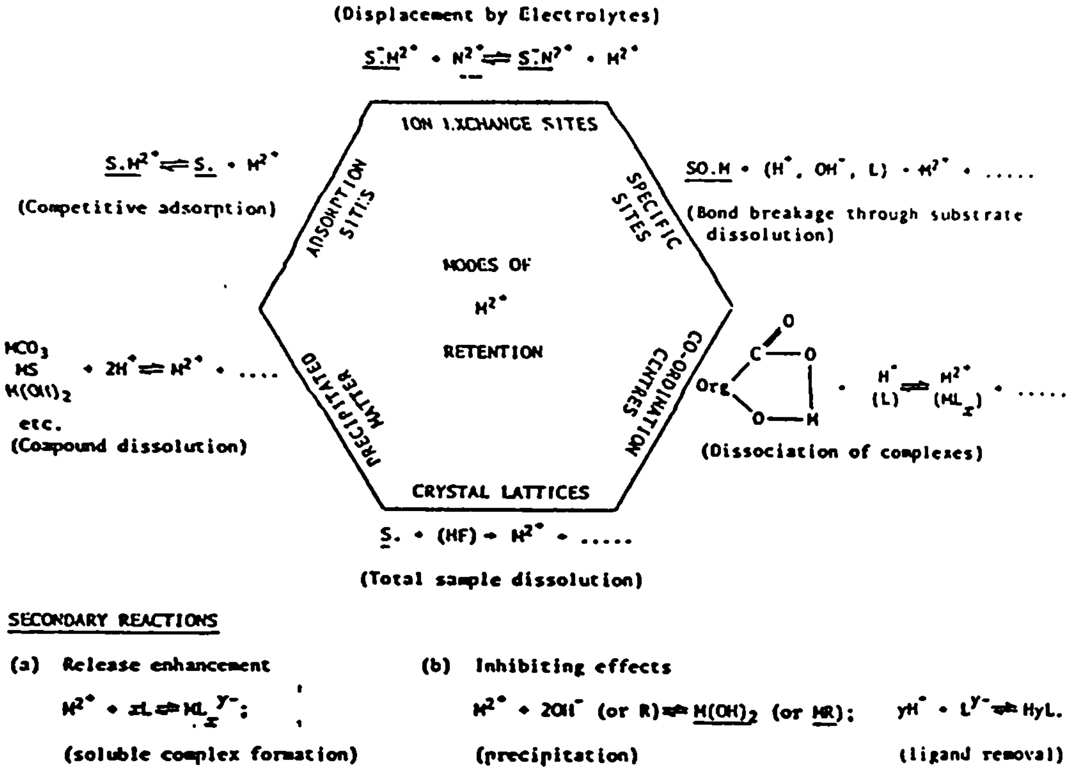


FIGURE 1 Summary of potential modes of M^{2+} retention in soils, with an indication of the chemical processes required to release the cation into an aqueous phase (symbol S = soil component).

organics in natural waters (Dursma,1965), the vast variety and low concentration of these molecules often make such an approach impractical. Instead of identifying and quantifying specific organo-metal complexes some workers have tried to determine the total capacity of a water sample to complex metal ions (Kunkal and Manahan,1973). Reported values in fresh water systems are 0.5 to 2.0 µmole/l. Other workers have taken an intermediate approach, dividing the ligands into several arbitrary groups depending on their molecular weight, composition, and the strength and/or reversibility of the metal-ligand bond (Chau and Lum-shue-Chen,1974; & Bradford,1972). They generally report at least two distinct types of complexes, one of which is very strong and reversible. Ligands forming these strong complexes probably belong to a general class multidentate, polymeric compounds known as humic acids. Gardner (1974) reported that humic complexes comprise most of the dissolved cadmium in several samples of river water and sewage effluent, and Matson (1968) and Reuter and Perude (1968) found humic acids to complex significant quantities of metals in several fresh water systems even in the presence of excess of major cations. However Stiff (1971) reported that amino acid complexes of copper are present in greater concentrations than humic complexes in both river water and sewage effluent.

In summary, the total dissolved metal concentration in aqueous systems may be many times that of the free aquo metal ion. Hydroxo- and carbonato-complexes are of major importance in fresh waters, and these two ligands, along with chloride, form the dominant inorganic complexes in sea water. Bi- and polysulphide complexes dominate speciation in sulphidic environments. Organic complexing agents are stronger but less concentrated and much more difficult to identify than inorganic ligands. They are probably important in many high-organic waters such as sewage effluent and the area of intense bioactivity. Counteracting the tendency of ligands to increase total dissolved metal concentrations are processes such as precipitation, adsorption and bio-uptake, which remove metals from solutions.

Most natural waters are significantly under-saturated with respect to precipitation of any pure heavy metal solid phase. This was first shown by Krauskopoff (1956) for 13 metals in sea water and has since been confirmed for cadmium and zinc in surface and ground-waters (Hem,1972). Pure phases do not exist in nature and since the solubility of a metal in equilibrium with co-precipitation phase is less than with a pure phase (Leckie & Nelson,1975), free metal concentrations may be controlled by the solubility of a co-precipitated mineral. It has been suggested that since cadmium and calcium are of approximately equal ionic radius, a co-precipitate of $CdCO_3$ - $CaCO_3$ may control cadmium concentrations in some systems (Fulkerson,1973). However, the explanation generally accepted for undersaturation of most natural waters is that the adsorption onto solids controls metal ion solubility (Kraskopof,1956; Jenne,1968). In some systems the two processes of adsorption and co-precipitation are indistinguishable (Dyck,1968).

Heavy metal concentrations on particulate matter are generally 10^2 to 10^4 times as large as they are in bulk solution. Despite the large concentration factors for sediments relative to dissolved species, the total amount of metal transported in solution may be equal to or greater than that by particulate in some systems (Preston et al.,1972; Perhac,1972).

Interactions between surfaces and metal ions in natural systems are extremely complicated since neither the exact form of the solid nor the speciation of metal is well known. The metal can undergo complexation reactions and the surface can be associated with biota, organic matter or other minerals. Niehof and Loeb (1972) found that all particulate matter acquires a negative surface charge when placed in sea water, regardless of its charge in pure electrolyte solutions. They attributed this to sorption of organic material on the surface. Such coating may affect heavy metal adsorption by altering surface charge, surface area, permeability to water and the selectivity of the surface for various metals (Kown and Ewing,1969). Gardner (1974) found that cadmium adsorbed on river mud is primarily associated with the organic (humic) fraction. DeGroot and coworkers (1964,1971) have suggested that in an estuary suspended river sediments release much of their adsorbed heavy metals as a result of desorption of organic matter, which then complexes the metals. Alternatively, trace metal solubility may be limited by adsorption onto hydrous oxides of Fe and Mn, which coat the surfaces of clays and other minerals (Jenne,1968).

In addition to characteristics of the adsorbent surface, the tendency of a metal ion to sorb is affected by its speciation in solution. The synthetic detergent additive NTA can chelate metal ions and has been reported to increase adsorption in some cases and decrease in others (Gregor,1972; Banat et al.,1974). Similarly chloride significantly decreases mercury adsorption onto amorphous iron hydroxide in pure system (Avotins,1975) but Cranston and Buckley (1972) found that the sediment-bound mercury increases in seaward direction. Sorption in estuarine environments is complicated by large gradients in organic concentration and salinity, the potential for ion exchange reactions and the possibility of particle flocculation (Muller and Forstner,1974).

Analysis of metal speciation in any natural system is further complicated by the presence of biota which may concentrate metal directly or alter the chemical forms of the metal by affecting the local water chemistry. Plankton can concentrate heavy metals by factors of 10^4 to 10^6 from ambient environmental concentrations (Mullins,1977). An example of biological activity altering speciation of metals indirectly was reported in Corpus Christi Bay, where reducing conditions during the summer led to precipitation of zinc and cadmium. The metals redissolved when oxidizing conditions are restored each winter (Holmes et al.,1974). Similarly Serne and Mercer (1975) found that more cadmium, copper, lead and zinc are released by shaking San Francisco Bay sediments in water under oxidizing than reducing conditions.

Thus, the transport of heavy metals through the environment is governed by an extremely complex set of biological, geological and chemical processes. The metal ions can associate with organic or inorganic ligands either in solution or on particulate matter. Solubility is increased by complexing agents and decreased by precipitation, adsorption and/or biological uptake. Other parameters such as salinity, redox potential and hydrology of the system, can also alter metal levels directly or indirectly.

2.2 Assessment of Heavy Metals Mobility

There is a tendency for elements introduced with solid waste material to be less strongly bound than those in natural compounds. Therefore, even relatively small proportions of anthropogenic materials may increase mobilization (and subsequent transfer to biota) of potentially toxic elements. Mobilization of metals i.e. enhancing their mobility, reactivity and biological availability, originates from changes in the chemical environment which are both affecting lower rates of precipitation or adsorption compared to natural conditions and active release of contaminants from solid materials. Five factors are important: (i) lowering of pH, either locally from mining effluent or regionally from acid precipitation; (ii) changing redox conditions, mainly after land deposition of polluted anoxic dredged materials, but also in aquatic systems (e.g., induced by seasonal variations of nutrient compounds); (iii) microbial solubilization by accelerating the oxidation of metal sulphides; formation of organometallic compounds by biomethylation; (iv) increasing salt concentrations, by the effects of competition on sorption sites on solid surfaces and by the formation of more soluble chloro- complexes with some trace metals; (v) increasing occurrence of natural and synthetic complexing agents, which can form soluble metal complexes with trace metals, that are otherwise adsorbed to solid matter.

Mobility of an element in the terrestrial and aquatic environment is reflected by the ratio of dissolved and solid fractions. Evaluation of the current literature indicates at least three major factors affecting the distribution of heavy metals between solution and particulate: (i) the chemical form of dissolved metals originating both from natural and civilization sources; (ii) the type of interactive processes, i.e. sorption-desorption or precipitation-controlled mechanisms (Solomons,1985); and (iii) concentration and composition of particulate matter, mainly with respect to surface-active phases. Effects such as reversibility and lack of knowledge on sorption kinetics may be important restrictions for using distribution coefficients in the assessment of metal mobility in rapidly changing environments, such as rivers, where equilibrium between solution and the solid phase is not achieved completely due to the short residence times. In practice, applicability of distribution coefficients may find further limitations from methodological problems. Simple pretreatment, solid/liquid separation technique and grain size distribution of solid material can influence strongly K_D factors of metals. Such effects also have to be considered, as well as the interpretations of in-situ processes, where the influence of reversibility usually are playing a smaller role than in the case of open-water conditions. The composition of interstitial waters is the most sensitive indicator of the types and the extent of reactions that take place between pollutants on waste particles and the aqueous phase which contacts them. Particularly for fine-grained material the large surface area related to the small volume of its entrapped interstitial water ensures that minor reactions with the solid phases will be indicated by major changes in the composition of the aqueous phase. In the framework of developing sediment quality criteria, the water quality seems to be particularly promising.

3.0 ROLE OF HYDROUS METAL OXIDES IN THE TRANSPORT OF HEAVY METALS IN THE ENVIRONMENT

3.1 Introduction

The term sediment refers to a complex mixture of three main components: clays, organic matter and oxides of iron and manganese. While the role of clays and biota in affecting the transport of pollutants is commonly recognized, the significance of iron and manganese is often overlooked. In view of the fact that the surface area and ion exchange capacities of iron and manganese oxides are large, the specific surface area and ion exchange capacity of freshly precipitated iron hydroxide are 300 m^2/g and 10 to 25 meq/100g respectively and the surface area of manganese hydroxide is 250 to 300 m^2/g (Fripiat,1952).

In order to understand the role that hydrous metal oxides may play in the environmental chemistry of heavy metal contaminants, it is essential to have some knowledge of the environmental chemistry of hydrous metal oxides. Parks (1967) summarized the factors controlling the sign and magnitude of the surface charge of the oxides and mineral oxides. He noted that the metal oxides exhibited ion exchange properties and the ion-exchange capacity of simple oxides arose from the existence of a pH dependent charge. He also noted that the charge on hydrous metal oxides is instrumental in determining the state of dispersion, rheology and the extent to which the solids act as ion exchangers for sorption sites. He also noted that it is possible that these materials could play important roles in the concentration of metals in natural water systems.

3.2 Sources of Hydrous Metal Oxides in Aquatic Environment

Hydrous metal oxides can arise from a variety of sources including the weathering of various mineral species. They enter natural water systems from both surface and ground water. Generally in a ground water system they would occur in the reduced oxidation states such as manganese (II) and iron (II). Upon contact with water which contains oxygen they oxidize to the hydrous metal oxides. The relative rates of oxidation of iron and manganese have been studied in detail. It has been reported by Stumm and Lee (1961) that while iron is oxidized by dissolved oxygen to the ferric form in the alkaline-neutral to slightly acidic pH range, manganese on the other hand requires much higher pH range for equivalent rates of oxidation. A considerable part of the manganese oxidation may take place at the surface of particles such as calcite where there is a microzone of higher pH. Also the manganese oxidation may be mediated to a considerable extent by micro-organisms.

In lakes with anoxic sediments which have reducing conditions it is generally found that both iron and manganese would tend to migrate in the sediments through the interstitial water until they come in contact with oxygen where a precipitation of the hydrous metal oxides should occur. Generally, the precipitation of iron would occur first. In lakes with anoxic hypoliminene, considerable concentrations of iron and manganese in their reduced state do build up in the water column below the thermocline. As a result of thermocline erosion, generally due to the high intensity wind stress, there could be continual production of hydrous metal oxides becoming part of epilimnion.

Since the hypolimnion often contains higher concentrations of iron and manganese in their reduced forms, thermocline erosion and leakage of hypoliminetic waters at the thermocline sediment interface may be the important source of freshly precipitated hydrous metal oxides in the surface water of lakes.

3.3 Environmental Chemistry of Hydrous Metal Oxides

Iron and manganese are among the major components comprising the crust of the earth and they are relevant constituents of many waters. They play an important role in water supplies, limnology and in oceanography. There have been numerous studies which point to the potential significance of hydrous metal oxides in influencing chemical contaminants in the environment. Jenne (1968) has proposed that the hydrous oxides of iron and manganese are the principal control mechanisms for cobalt, nickel, copper, lead and zinc in soil and fresh water sediments. He states that the common occurrence of these oxides as coatings allows them to exert a chemical activity far in excess of their total concentrations. He further indicates that the uptake or release of these metals from those oxides is a function of factors such as increased metal ion concentration, pH and the amount and the type of organic and inorganic complex formed in solution.

Jenne (1968) claims that the information available on the factors that control copper, nickel, cobalt, lead and zinc in natural waters suggests that the organic matter, clays and precipitation as discrete oxides or hydroxides can not explain the aqueous environmental chemistry of these elements. According to Jenne (1968), this explanation must include, as one of the dominant factors, the environmental behaviour of iron and manganese. The primary basis for Jenne's remarks is the literature on the behavior of these metals in the soil system. It is certainly reasonable to extend this behavior to the aquatic sediment systems, since they are similar to some soils. There are significant differences between sediments and soils that must be considered in any specific location and care must be exercised in extrapolating soil chemistry studies to the area of aquatic chemistry of sediments.

Clay minerals and some other mineral species have a significant cation exchange. It is sometimes stated that they could play a dominant role in the transport of heavy metals. However, it is doubtful that cation exchange capacity of layer silicates, such as clay minerals, play a significant role in the heavy metal transport for several reasons. First, the cation exchange capacity represents a small part of the adsorption capacity of neutral water particulate matter for cations. Another factor to consider is that competing for cation exchange sites with heavy metals of interest are the bulk metal species such as calcium, magnesium and sodium which occur at concentrations many times those of the heavy metals.

Since in general cation exchange reactions have distribution coefficients of approximately the same order of magnitude for the various metallic species, it would be expected that calcium and magnesium would be the dominant ions occupying the cation exchange sites with very few of them being covered by metal ions of the heavy metal type. Jenne (1968) has noted that there is little relationship between the cation exchange capacity of soils and the fixation of heavy metal in the soils. Morgan & Stumm (1964) found that the distribution coefficients for heavy metals on freshly precipitated manganese dioxide was greater than for alkaline or alkaline earth metals. Therefore, there could be a preferential sorption of heavy metals on hydrous metal oxides even in the presence of large amounts of other cations.

It should be noted that when considering the sorption capacity of mineral fragments for heavy metal species, consideration must be given to the possibility of hydrous metal oxide coating on the surface of these particles which would in turn play a dominant role in the chemistry of heavy metals.

It is important to emphasize that the control of heavy metals by mineral fragments with hydrous oxide coatings may actually be a tertiary or possibly a quaternary system where organic matter in the form of colloidal compounds or dissolved species or a combination of both may actually be involved. Few studies have been done on tertiary systems of this type involving heavy metals. Wang et al. (1972) have conducted some studies on tertiary systems involving clay minerals, organics and pesticides. It was found that the sorption of pesticides on clays was enhanced with the presence or absence of certain types of organic compounds. In one case, a certain type of organic would enhance the sorption of parathion on montmorilonite, while another organic would inhibit parathion sorption on montmorilonite.

One of the most pronounced examples of the sorption capacity of hydrous metal oxides for trace metals is found in the manganese nodules from the oceans (Goldberg,1960). Numerous studies have shown that these nodules contain large amounts of heavy metals. The concentration of some metals in these nodules is sufficient to cause serious consideration of nodule mining for the recovery of heavy metals. While the exact mechanism of incorporation is not known, it is likely to involve a sorption of metal ions on the hydrous metal oxides. It was proposed (Jenne,1968) that the hydrous metal oxides of iron and manganese are nearly ubiquitous in soil and sediments, both the partial coatings on other minerals and these oxides act as a sink and modes of transport for heavy metals in the environment but the quantitative magnitude of this role is not known for a variety of natural water conditions.

It is clear that as greater emphasis is placed on the control of heavy metals in the environment by water pollution control regulatory agencies, a much better understanding of the interactions between heavy metals and hydrous metal oxides must be available in order to affect technically sound and economically feasible control programmes. It is necessary to place the environmental movement in its proper perspective i.e., to determine the true affect of various materials contributed to the environment, to determine the economic impact of removing these materials from waste effluent, and to compare these costs with the benefits attained by their removal.

4.0 CLAY MINERALOGY AND ADSORPTION CHARACTERISTICS

4.1 Introduction

The clay minerals may be broadly described as hydrous alumino-silicates, although other metals are usually present in smaller quantities. In the structural classification scheme most are phyllosilicates, displaying a continuous sheet-like structure. Sheets are composed of either a two dimensional network of aluminum atom surrounded in an octahedral geometry by oxygen atoms or hydroxyl groups or of two dimensional network of silicon atoms surrounded in tetrahedral geometry by oxygen atoms or hydroxyl groups (Figure 2) (Grim,1968). These two types of sheets are stacked upon one another in one of two ways. The two types of sheets regularly alternate with one another to form the asymmetric structure of kaolinite, a clay mineral with an ideal formula $Al_4Si_4O_{10}(OH)_8$ or a series of larger layers consisting of an octahedral sheet sandwiched between two tetrahedral sheets may be stacked upon each other yielding the structure of montmorilonite with the ideal formula $Al_4([Si_4O_{10}])_2(OH)_4$.

There are many other clay minerals but most are based on one of these two stacking schemes, with differences in the geometry of stacking and substitution of other metals for aluminum and silicon creating unique properties. The two-sheet layers of kaolinite are more strongly bound to one another than the three-sheet layers of montmorilonite because oxygen atoms face hydroxyl groups in the kaolinite structure while oxygen atoms face another oxygen atom

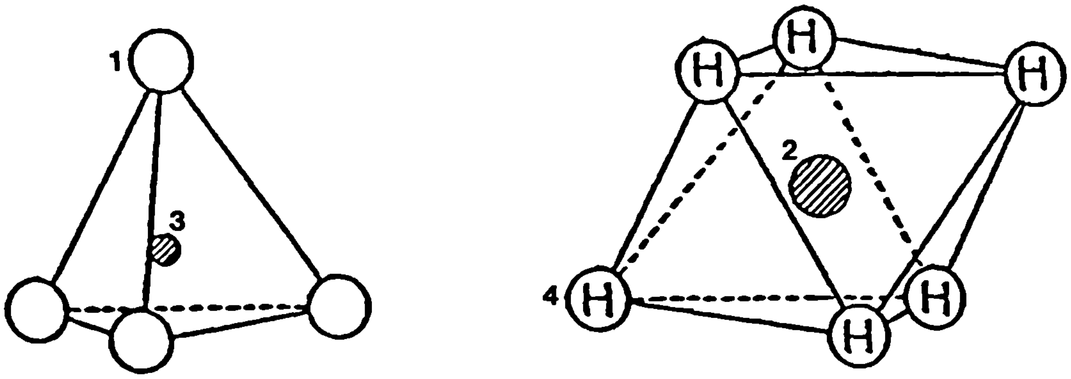


Figure 2. Diagramatic sketch showing tetrahedral and
octahedral units.
1- oxygen
2- aluminium, iron etc.
3- silicon
4- hydroxyl

in the montmorilonite structure. Hydrogen bonding in kaolinite makes cleavage along the layer more difficult than for montmorilonite (Ross & Kerr,1931).

Substitution of other cations of proper radius for silicon and aluminum atoms occurs much more extensively in montmorilonite than in kaolinite. The more tightly bound layers of kaolinite allow only a minimum of isomorphous cation substitution. In montmorilonite structure one may observe up to 15% substitution of Al^{+3} for Si^{+4} in the tetrahedral sheets, and occasionally complete substitution of Mg^{+2} and Fe^{+2} and less commonly Zn^{+2} ,Ni^{+2} or Li^{+1} for Al^{+3} atoms of the octahedral sheets. Whenever a cation of lesser charge structurally substitutes for cation of greater charge the clay is left with what may be described as either an excess of negative charge or a deficiency of positive charge depending on how the charge imbalance is relieved. For clays based on the montmorilonite structure three main means of charge compensation may be found. Cations may be directly adsorbed onto the surface of individual layers. Secondly, cations may occupy lattice sites not occupied by Al^{+3} in the octahedral sheets. This filling of sites is possible because only 2/3 of the available Al^{+3} lattice sites are occupied in the ideal montmorilonite structure. Thirdly, O^{-2} species may be altered to OH^- Surface adsorption of cations is always involved to a certain extent, thus explaining the high capacity of ion exchange typical of a montmorilonite structure.

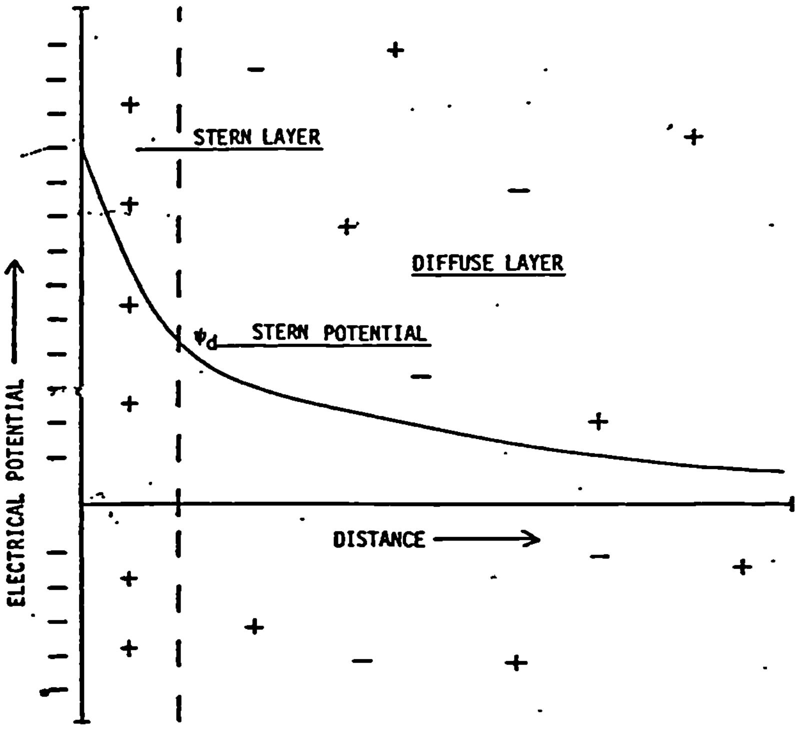
A cation particularly well suited to balance negative surface charge in montmorilonite is K^+. Its large size allows it to fit quite snugly between layers. If most of the charge imbalance in montmorilonite clay is due to substitution in the tetrahedral sheets, negative charge is localized near the surface of each 3-sheet layer and potassium ions in the inter-layer region are bound very tightly. Clays with successive layers held together by K^+ are referred to as illite, $K_{0-2}Al_4(Si_{8-6}Al_{0-2})O_{20}(OH)_4$ representing an idealized formula. Illite appears to represent a transition between montmorilonite and muscovite, $[K_2Al_4(Si_6Al_2)O_{20}(OH)_4]$, although it has been suggested that illite is merely a mechanical mixture of these two minerals. The important point here is that K, tightly bound between layers in illite or muscovite minerals, are not as available for ion exchange as are more loosely bound cations associated with montmorilonite, where charge imbalance originates more in the octahedral sheet and is more diffuse at a layer surface.

The formation of clays during the weathering of aluminosilicate rock is substantiated by geologic relationships between two substances, but the exact nature of the chemical processes forming clays are not known. Rather extensive bond breaking and formation is necessary to convert the chain structures of pyroxenes and amphiboles into the sheet characteristic of clays. The behavior of clay minerals in natural waters is related to particle size. The attendant large surface area of clay makes surface adsorption of ions from solution very efficient per unit weight of clay. The overall charge of colloidal clays is always negative, the result of imbalance produced by isomorphous substitution and by broken bonds. Since clay particles are fragments of a layer structure extending continuously in the crystallographic plane, the edges of fragments contain species whose valency satisfaction was interrupted by bond breaking. Unsatisfied silicon and aluminum valencies actually produce localized areas of positive charge located on particle edges (Faust & Hunter,1967). In response to the overall negative charge of clay colloids, cations in natural waters are adsorbed onto surface sites.

crystal structure

The concept of an electrical double layer was popularized by Gouy (1913 Cit: Worral, 1968). The negative surface charge attracts a tightly bound layer of counter ions called the Stern layer and the potential at this point is called Stern potential. Beyond this layer is a diffuse layer of both cations and anions, which together comprise the electrical double layer (Figure 3). In addition to the ions, the positive pole of the water molecule dipole is attracted to the colloidal surface. This layer of tightly bound water molecules does not generally extend much beyond the Stern layer and the potential at its boundary is called the zeta potential. The value of the zeta potential will vary with the valency and the concentration of counter ions present in solution. High concentration of any cation tends to lower the zeta potential, as do di- and trivalent cations relative to monovalent cations.

The law of mass action has some uses in describing the transfer of ions between the electrical double layer of colloidal clays and a bulk solution. The



ELECTRICAL DOUBLE LAYER = STERN LAYER + DIFFUSE LAYER

FIGURE : ELECTRICAL DOUBLE LAYER ABOUT THE SURFACE OF A NEGATIVELY CHARGED PARTICLE IN AQUEOUS SOLUTION (MODIFIED FROM WORRALL, 1968).

ability of colloidal dispersion to remain in that state depends on the mutual repulsions of particles due to their zeta potentials. Particles possessing a low zeta potential will be able to approach close enough for van der Waals forces to be effectively exerted and cause the particles to flocculate and eventually settle out of solution. The addition of high concentrations of an electrolyte generally lower the zeta potential sufficiently for flocculation to occur. Such a process occurs when clays suspended in fresh waters reach the oceans, with its increased ionic strength. Montmorilonite flocculated in such a way that they respond to the relatively high K^+ activity in ocean water and slowly convert to illite. Oxide surfaces could be charged through reactions with $OH^-$and H^+ in solutions. These reactions are of type:

$\underline{X}OH + H_2O$ .... $\underline{X}O^- + H_3O^+$ $XO^- + H^+$

$\underline{X}OH + H_2O$ .... $\underline{X}OH^+_2 + OH^-$ $X^+ + OH^-$

where underlining indicates the solid phase, $\underline{X}OH$ represents the hydrated surface and X is the central metal atom of the oxide (Si in SiO_2).

4.2 Pathways and Mechanisms of Trace Metals Incorporation into the Sediments

4.2.1 Pathways to the Sediments

Trace metals reach the sediments in three principal ways: (i) in or on the particles which settle to the bottom, (ii) in or on the particles which are transported along the bottom, and (iii) by the sorption of dissolved metals from waters in contact with the sediments.

The sedimentation of particles is invariably the most important pathway and three classes of particles may be distinguished: detrital, biogenous and precipitated. It has been suggested that detrital particles may carry heavy metals within the crystal lattice, adsorbed on the surface, in the exchange sites of clay minerals and the surface coatings formed by hydrous metal oxides or organic matter. Similarly, particles of biogenous origin may contain heavy metals within inorganic skeletal materials, complexed to organic matter, and in coatings of hydrous oxides which may form on particles. A third class of sedimentary particles are precipitated such as calcium carbonates, hydrous oxides and sulphides, and it has been proposed that these carry heavy metals adsorbed on the surface, as co-precipitated material, and as metal compounds precipitate as discrete particles.

Heavy metals may be considered to be either (i) bound within particles (this may be taken to include metals complexed to organic matter, metals in exchange sites and co-precipitated) or, (ii) bound to the surface of particles by adsorption, or (iii) located in a surface coating deposited on the particles. The limited evidence available e.g. Gibbs (1977); Forstner (1977), suggest that most metal is held within particles or in hydrous oxide coatings rather than as simple adsorbed layer.

As particles settle through the water column they may be partially dissolved by bacterial attack (Price & Skei,1975) or changes in the chemical environment. Those that survive and reach the sediments may be further decomposed by diagenetic processes (Price,1976). Others will be ingested by aquatic organisms and subsequently attacked by the gut fluids in the animal (Luoma & Bryan,1978). Thus, the degree to which a given particle resists chemical or biological dissolution has an important bearing on the fate of its constituent heavy metals.

Another pathway involves direct uptake by sediment particles of dissolved metal species. Uptake can occur from the water above the sediment surface or from interstitial waters diffusing upwards from below the sediment surface. The most convincing evidence for direct uptake is the observation that ferromanganese nodules can form in areas which are swept clear of accumulating bottom sediment (Damiane et al.,1977). However, trace metals are not necessarily enriched in such nodules. It may be that the uptake across the sediment-water interface is not only a chemical process. For example manganese oxidizing bacteria attached to the inside surfaces of hydroelectric pipelines are known to produce insoluble manganese deposits thick enough to upset streamline flow (Marshall,1978). Jenne and Wahlberg (1965) studied the enrichment of trace metals in iron oxide compounds of stream sediments. Cutshall (1967) found iron oxides to be the most important single sediment component in the retention of chromium in sediments from the Columbia Rivers

4.2.2 Incorporation into the Sediments

Particles deposited on the bottom will at first sit loosely at the sediment surface. Sometimes, an easily disturbed 'flock' of fine probably biogenous material collects just above the interface (Emery et al.,1975). Eventually, new sediment buries what remains of the old, which is then incorporated on a more permanent basis into the bulk of sediment. In the times between settlement and burial newly arrived sedimentary particles may be affected by a number of processes, viz mixing, resuspension, decomposition, dissolution and precipitation.

4.2.3 Mixing

Currents at the sediment interface move, sort and mix the surface layers. Burrowing organisms also stir sediments by: (i) pumping interstitial water out of the sediment and bringing in oxygen enriched water; (ii) transporting particles to the surface and into deeper layers (Peter,1977).

4.2.4 Resuspension

In shallow lakes and coastal basins winds are often of sufficient strength and duration to cause resuspension of the bottom sediments and consequent transfer of nutrients to the water column (Ryding & Forstner,1977). The fate of heavy metals present in the resuspended particles has not been determined in the field, although laboratory experiments suggest that anaerobic organic rich river sludge releases heavy metals on oxygenation (Muller & Schleichert,1977). Similarly, samples of Los Angeles harbor sediments mixed with sea water released more lead, zinc and cadmium as the conditions were made progressively more oxidizing (Lu and Chen,1977).

4.2.5 Decomposition

Physical processes such as hydraulic mixing crush and fragment the larger particles in sediments, ultimately producing rounded detrital grains and very fine shell fragments. However, biological decomposition is probably more important as far as heavy metals are concerned. There appears to be two processes: (i) a fairly rapid release of metals (may be from body fluids) soon after the death of an organism (Price & Skei,1975); and (ii) a slower release of metals from the degradation of more resistant structures. A variety of microorganisms decompose carbohydrates, hydrocarbons, proteins and amino acids (Kuznetsov, 1975) but the fate of associated heavy metals is not well understood. It is generally assumed that most of the metal is released into the solution rather than buried with the residues (Jackson,1978).

Although in the overall process of decay, organic matter may release heavy metals at any stage. In the process, the organic detritus is apparently capable of sorbing metals if placed in contact with the solutions of metal salts.

4.2.6 Recycling Through Organisms

Living organisms can temporarily take up heavy metals from other sediment components and later return those metals to the sediments via faeces and decaying tissues and skeletal materials (James,1978). This recycling of metals within the sediments can also involve transfer up benthic food chains, e.g. from organic matter to bacteria to worms and them return on the death of the worms (Ireland,1977). Alternatively if the worms were eaten by bottom feeding fishes their constituents heavy metal would be removed from the sediments. Presumably that portion of metals which is incorporated into the hard parts of organisms is recycled more slowly than that in the soft and easily decomposed parts. Thus the ability of molluscs to fix lead in their shells and of fish to fix lead in their bones should act to reduce the recycling of lead through organisms.

Benthic plants which take up metals through their roots may in so doing recycle metals within the sedimentary compartments. On the other hand those algae which sorb metals through their fronds transfer metals from the water column to the sediments via their decay products but will not be necessarily be involved in the recycling of those metals.

4.2.7 Dissolution and Precipitation

Oxidation of organic matter by biological agents cause a downward depletion of oxygen in sediments. Iron and manganese which occur as iron hydroxide and manganese oxides under aerobic conditions are reduced to soluble iron and manganese ions. Upward diffusion of ions out of the reduced zone leads to the precipitation of iron and manganese at or near the sediment-water interface.

A similar cycling between insoluble oxidized and soluble reduced phase is not to be expected for lead, zinc, copper and cadmium. However, the metals may be temporarily released from dissolving ferromanganese oxides before further reaction with anions such as sulphides, carbonates and chlorides or with organic complexes. Nissenbaum and Swaine (1976) concluded that dissolved organic matter plays an important role in the process of dissolution and precipitation. They proposed that polymeric organic material in interstitial water, leached metals such as copper and zinc from mineral phase in sediments and subsequently reprecipitated the metals as metal rich humates.

In reducing environments sulphide ions compete with organic matter for the available metals, a portion of which may be present as precipitated sulphide. Lead, copper, zinc and cadmium sulphides are not expected to be remobilized once formed in anoxic sediments (Price,1976). Extraction tests suggest that they are certainly less available than metal-organic complexes (Jackson,1978). However, if the sulphides were transferred to an oxidizing environment by bioturbation or resuspension some dissolution could occur.

4.3 Bioavailability of Sediment Bound Metals

The amount of metal taken up by living organisms, living and feeding in the sediments, is obviously a crucial environmental question, more important ultimately than the actual concentration of metal in the sediment. However such is the complexity of biological systems that a simple relationship between the concentration and nature of sediment-metal and its bioavailability to organisms in the same ecosystem is not to be expected. There has been some progress in identifying, for particular organisms, which components of the sediment contain the most readily available heavy metals.

Luoma and Bryan (1978) compared the concentration of lead in the soft tissues of the deposit feeding bivalve (Scrobicularia plana) in various English estuaries with metal concentrations in extracts of sediments. They found that the biological availability of lead was strongly influenced by the level of readily extractable iron and lead concentrations in bivalves were fairly well predicted from the Pb/Fe ratio in hydrochloric acid (1N) extracts of surface sediments, despite wide variations in the particle size, organic carbon, calcium carbonate and salinity from one estuary to another. They concluded that iron oxide-bound lead was less available than other forms of lead in the sediments. However other metals behaved differently; their uptake was not controlled by the relative proportion of extractable iron in the sediment but more by the extractable humic substances. The same dependence on humic substances was not found for a similar bivalve, *Macoma balthica.* Biological systems are so complex that a simple relationship between the concentration and nature of sediment-metal and its bioavailability to various organisms in the same ecosystem is not to be expected. Metal concentrations in the different types of organisms can vary greatly. The various trophic levels of several species must therefore be simultaneously investigated, since the metal concentrations within the certain level can fluctuate considerably according to different dietary habits.

In addition to its position within the food chain, the morpho-physiologic structure of a particular species can also help account for the differences in metal content encountered in different species, since the structure and function of the organs in contact with the contaminated medium can be instrumental in governing the metal contents. thus, an important aspect of metal enrichment is whether respiration occurs via gills, skin or atmospherically.

5.0 BIOLOGICAL AVAILABILITY OF METALS TO AQUATIC ORGANISMS

5.1 Introduction

To have an impact on aquatic organisms, metals must be in a form that is biologically available to them; only in this form do the metals inflict a toxic action on the organisms and/or are bioaccumulated by them. For this reason it makes little sense to consider that the total amount of metal present in the aquatic environment, whether in water or sediments, is available to cause damage to aquatic organisms or to the aquatic ecosystem. The effects of disposing mine tailings into the sea from a copper mine were being examined (University of British Columbia, Canada,1981), if total copper is a criterion of biological hazard, all the ships in Vancouver Harbor would have to be regarded as a threat to the marine ecosystem, because of the copper-containing brass propellers; a ship's propellers can only be regarded as biological hazard to the extent that copper, zinc, tin, and other metals that constitute the alloy known as brass, are leached into the water in a form that is biologically available to the organisms. The biologically available form of metal is usually the dissolved ionic form, but not all ionic forms pose the same biological hazard. Metals in pure form are only available to aquatic organisms if they become oxidized (corrode) and their oxidation products are soluble in the water.

Metals in particulate form, both suspended in the water and in the sediments, are seldom available directly to aquatic organisms. Such metals may be either fixed in an organic medium, for example, contaminated plankton, or in an inorganic matrix, e.g. mine tailings. The only exception to their biological unbioavailability is when the particulate metals are ingested by aquatic organisms and become solubilized in the acidic juices of the gut. Often, these particulate metals are excreted essentially unchanged after they are consumed by such benthic organisms as bivalves and worms, which are usually filter feeders consuming plankton or detritus feeders ingesting sedimentary particles.

5.2 Natural Processes Releasing Metals from Minerals

Metals in the mineral form can be leached into water chemically and microbiologically. Sulphide minerals exposed to atmospheric oxidation are converted to sulphates, and on combination with water, produce sulphuric acid. This acidic condition leads to more rapid leaching of the metals into the water. Leaching of metals can be aided by appropriate metal-leaching bacteria, such as ***Thiobacillus ferrooxidans***, which perform best under acidic conditions. The presence of the sulphide mineral pyrite (FeS_2) is generally recognized as the main source of acidity in acidic mine drainage and can support microbiological leaching. If an ore is designated as 'acidic', these micro-organisms can rapidly oxidize the reduced form of iron and sulphur, generating sulphuric acid and releasing the metals. Bacteriological leaching is one of the aspects of biotechnology that is extremely important to the mining industry. This is an important process of releasing metals from the ore efficiently. Drainage water from these bacteriologically-leached ores can be quite acidic, as well as containing high metal concentrations. Drainage water at a former copper mine at British Columbia has been found to have a copper concentration of 200 µg/g (Forstner & Wittmann,1983). Such metal-rich acidic water can be extremely damaging to freshwater ecosystems. In the marine environment the acidic condition can be soon neutralized by weak-acid salts present in the seawater. The metals may remain in solution, however, and they can be readily available for biological uptake. Some of the metals may be scavenged by particulate material in the water and deposited in the sediments.

Metals present in runoff waters in particulate form, arising from erosion of mineralized areas of a drainage basin, normally contribute rather little biologically available metals to either freshwater drainage or to the seawater with which it eventually mixes. Very small amounts of the metals may be leached directly into the water. Any further contributions of metals from the particulate phase to the water and organisms would depend on biogeochemical activity in the sediments and on the release of metals in the gut of filter feeders and detritus feeders.

5.3 Biogeochemical Processes in the Sediments

Metals deposited in the sediments are usually fixed there unless certain natural or anthropogenic changes mobilize them. The natural changes arise from the digenetic process, which is the sum of the normal biogeochemical reactions that can take place in the sediments. Man-made effects may include addition of inorganic or organic substances to the sediments through dumping, exposing anoxic sediments to oxidation by aeration through dredging, and altering flow and mixing of water over sediments by installing various types of structures.

A microbiological process affecting metals in sediments has been of much concern ever since the Minamata episode in Japan, where persons consuming seafood contaminated by mercury were afflicted by a serious neurological disorder that sometimes ended in mortality or permanent disability. The cause was found to be a form of organic mercury that could be produced by bacteria from inorganic mercury in sediments. There has been evidence of methylation of other metals (e.g. arsenic, selenium, tin and lead) (Forstner & Whittmann,1983) in sediments. So far, however, there has been no indication that a serious threat to the health of seafood consumers is posed by organometals other than mercury in marine sediments. There continues to be a vigil for organic forms of metals in sediments, nevertheless, because of their higher solubility in seawater than inorganic forms and potential bioavailability to marine organisms.

5.4 Mine Tailings

Metals in an inorganic matrix, such as mine tailings, appear to vary in their solubility from one area to another. This may, in part, be related to the nature of the matrix in which the metals are fixed. For example, metals in quartz matrix are less likely to be leached from a mineral than if they are present in a more soluble matrix, such as carbonate. In the case of mine tailings, it appears also that the physical and chemical treatment to which the ore is subjected can make a difference in the extent of leaching of metals when the tailings are discharged in to the seawater.

A comparison of the leaching of metals from tailings of two base-metal mines, a zinc-lead mine on the west-central coast of Greenland and a copper mine on the west coast of Vancouver Island, shows a great difference between the two (Waldichuck & Buchanan, 1980). Very little copper in tailings from the latter mine appears to leach into the seawater of Rupert Inlet, where the tailings are discharged, or is bioaccumulated by marine organisms. On the other hand, lead appears to have entered substantial concentration in the seawater at Afgfardlikavsa fjord in Greenland and has been bioaccumulated by such organisms as mussels. The solubilities of the mineral matrices in the two mines may hold part of the answer to the differences in the release of metals into the seawater and biological uptake.

5.5 Sewage Sludge and Dredge Spoils

Sewage sludge often contains high concentrations of metals stemming from industrial wastes and laboratory effluent entering the municipal sewerage systems. Such sludge also contains a large amount of organic matter. As a general rule, the organic constituents bind the metals in the sludge into a form that renders them unavailable biologically. This may occur through chelation of the metals by organic compounds or by simple adsorption.

Dredge spoil is perhaps the material that is dumped in greatest volume into the ocean. Depending on where it originates, dredgate may be quite clean or it may be heavily contaminated. If industry has been discharging wastes of any kind nearby, one can expect assorted contaminants in the sediments. Estuaries of rivers, which have mining operations or other metal-extractive industries upstream, are notorious for high metal concentrations in their sediments. These sedimentary metals are biologically available in varying degrees. A high organic content in the sediments will usually ensure that the metals are quite firmly fixed in the sediments and are not freely available to the aquatic biota. If the metals are present in rather refractory particulate matter, they are also not likely to be readily leachable and readily available to the organisms.

5.6 Effects of Water Characteristics

Seawater characteristics can alter the rate of release of metals from particulate material and the uptake by aquatic organisms. As a general rule, hydrogen ion, as represented by pH, plays an important role in the rate of release of metals into water. If the water is acidic with a low pH, metals are released much more rapidly than when the water is more alkaline and pH is comparatively high. Fresh water, especially if it is soft, can rapidly undergo changes in pH by addition of acids or alkalies, because it contains very little dissolved material and is relatively unbuffered. As fresh water becomes increasingly more acidic, it has capacity to bring more and more metals into solution. Seawater, on the other hand, contains a relatively high concentration of dissolved materials, especially weak-acid salts such as borates and bicarbonates, which give it a high buffering capacity. It undergoes little pH change even with large additions of acids or alkalies. Consequently, there is little impact from acidic effluent on the solubility of metals in seawater of normal salinity (30-35‰). By and large, leachability of metals from solid materials, such as dredge spoils, increases with declining salinity. It is not certain whether this relationship is related to the actual salt content of the water or the pH that is controlled to some degree by weak-acid salts, as reflected in the salinity.

Temperature is normally directly related to the dissolution rate of metals. The well known exception to this rule is calcium carbonate, which tends to be more soluble at lower temperatures and precipitates out at higher temperatures, as illustrated by the scaling effect in kettles in which hard water has been repeatedly boiled. Insofar as metal uptake by marine organisms is concerned, the metals are bioaccumulated more rapidly with increasing temperature, in as much as the metabolic rate increases with temperature.

Dissolved oxygen in the water has an effect on metal dissolution in that it controls the redox potential. Normally, a higher dissolved oxygen concentration contributes to a higher redox potential and greater dissolution of metals, except for iron and manganese, into water. When the dissolved oxygen concentration diminishes, and hydrogen sulphide is formed, the redox potential decreases and eventually goes into a negative state. Most metals, except for iron and manganese, have insoluble sulphides, and a large decrease in redox potential ensures that they become immobilized in the sediments.

5.7 Mode of Uptake by Aquatic Organisms

Aquatic organisms may take metals through food or water. Studies that have been done on some invertebrates show that about equal amounts can be taken in by both routes. Different species have different rates of bioaccumulation and the sites of major concentration may differ from one species to another. Cadmium accumulates in the hepatopancreas of the American lobster ***Homarus americanus*** (Uthe & Zitko,1980). The liver and kidneys are usually the sites of major concentrations of metals in fish, although mercury tends to be present in relatively high concentrations in the muscle of fish. There is no evidence of biomagnification of metals through the food chain except for mercury. For any given species, there may be a difference between male and female in the rate of uptake and release of metals. The age of an animal can also make a difference in rate of uptake. These kinds of problems were well recognized in the 'Mussel Watch' (Goldberg,1980).

Certain metals, particularly cadmium, have been shown to combine with metal-binding proteins, such as metallothionein, in a detoxification process. To a certain limit, the organism can synthesize more of the metal-binding protein to cope with the additional metal ingested. This process explains, in part, the apparent 'acclimation' of certain organisms to moderately high levels of metals in their environment. While this process of detoxification apparently protects in some degree the organism ingesting a given metal, it does not protect predators, including man, from an excessive intake of the metals.

Because certain metals are essential elements in the nutrition of most animals, some marine organisms have developed a capability of controlling their intake. This capability can confound any relationship that one may try to develop between the concentrations of a metal in the water or sediments and in the tissues of the exposed organisms.

5.8 Measurement of Bioavailablity of Metals

At the present time, there is no substitute for chemical analysis of the tissues of the exposed aquatic organisms for metal concentrations, if one wishes to determine the biological availability of metals at a given site. Measurement of the sublethal biological effects of metals on the local population of organisms is confounded by physiological adaptation to certain metals that can occur at least in some species. Bioassays on organisms that have not been acclimatized to the conditions of the area in question often yield results that are very different from those of bioassays with metal-adapted organisms (Uthe & Zitko,1980).

Ideally, chemical tests would be desirable to identify and measure the concentrations of metals in water and sediments that are biologically available. The dissolved forms of metals in seawater are generally considered biologically available, but this bioavailability may vary in degree from one ionic species to another. Although measurement of the dissolved species of metals in seawater can be carried out quite routinely, albeit not for individual ionic species, much skill and fairly sophisticated analytical equipment are required to achieve the kind of precision, accuracy and sensitivity in metal detection that would make the data useful.

The real chemical test of biological availability, however, comes in the analysis of particulate material containing metals. A simple leaching test would consist of exposing a metal-containing material, such as mine tailings for example, to seawater and measuring the metal concentration in seawater before and after a given period of exposure. This would provide some indication of the dissolution of the particulate metal directly into the seawater and of the bioavailability of the metal for uptake by marine organisms through water routes.

For a measure of the availability of the particulate metal, when ingested by detritus or sediment feeders, it is necessary to provide an extraction that would simulate that which occurs on exposure of the particulate metal to the acidic gastric juices in the gut of the organisms. Assorted weak-acid extractions have been essentially applied to simulate the effect of gastric juices in the gut of a detritus or sediment feeder.

It is admitted by most aquatic biogeochemists that no single chemical extractant can predict accurately the exact bioavailability of any given metal to a given species. Moreover, there is no chemical way to routinely distinguish the metals coming from anthropogenic sources from those arising from natural sources.

6.0 ENVIRONMENTAL CONCERNS ABOUT CONTAMINATED SEDIMENTS

6.1 Introduction

Contaminated sediments are an important aspect of hazard assessments in aquatic systems. It is generally felt that the sediments provide beneficial effects in terms of water quality improvement through the adsorption of pollutants from the water column but contaminated sediments may also result in adverse effects. There is increasing evidence that illustrates the importance of the sediment-associated contaminants to direct toxicity and bioaccumulation in benthic organisms (Salomons,1978) and to continued water quality problems following source control due to release of previously bound contaminants from sediments.

The environmental hazard of chemical contaminants present in the aquatic environment is largely related to exposure to bioavailable forms of contaminant. The available forms will be determined by the net result of interacting phenomena governing the environmental partitioning. For example, sorption, hydrolysis, photolysis, biodegradation and volatilization processes may be important for an organic contaminant while adsorption, hydrolysis, complexation, chemical precipitation and oxidation-reduction processes may be important in the environmental fate of toxic metals. The extent to which each process influences the exposure concentration will largely determine the actual toxicity of the chemical in receiving waters. For the majority of metals of interest with respect to aquatic hazards, the interactions of dissolved forms of metals with solids are major fate-influencing processes.

6.2 Environmental Significance

To provide the appropriate level of protection for aquatic life and other uses of the resource, it is important to be able to predict the environmental distribution of important metals on spatial and temporal scales and to do so with particular emphasis on the water column concentrations. Regulatory levels reflected in water quality criteria or standards are based on water column concentrations. Predicting water column concentrations requires a consideration of the interactions of water column contaminants with both bed sediments and suspended particulates as critical components in the assessment.

Contaminants which have been associated with fresh water sediments have a variety of both temporary and permanent resting points in streams, rivers, lakes, reservoirs and estuaries. It is generally known that contaminated sediments are located throughout a stream reach which is below chemical loadings from particular sources, such as industrial discharges, domestic waste waters, mining and milling, metal finishing, landfill leachates or contaminated groundwater discharge (Brian,1988). Reversing currents in lakes and estuaries may disperse contaminated sediments throughout the water body.

The concentration of a contaminant observed at a particular point in response to these chemical loadings reflects not only the loading of the chemical relative to the water residence time and important processes that cause association of the contaminant with the sediments but also the dynamics of the natural environment and sediment transport processes. Consider a contaminated river entering a lake system (Amur River in lake Baikal in USSR, for example), the lake water quality will reflect the loadings from the river and the movement of contaminated sediment and dissolved contaminant in response to hydrodynamics and the transformation process. Sediment concentrations throughout the lake will reflect the loading and the effects of river mouth sedimentation as well as wind and wave action. The concentration of contaminants in the sediments is highly site specific and dependent on the physical, chemical and biological factors affecting sediment-water exchange. While it is difficult to describe sediment mass and contaminant concentration in dynamic systems in a very detailed manner, it is possible to describe the major processes taking place and the environmental response under the more steady conditions that may exist. A scientific basis to aquatic hazard assessments requires an understanding and description of the important fate-influencing processes and their relative concentration to controlling exposure from water, sediments, interstitial water and food. Current efforts to model the fate and transport of contaminants in the aquatic environment are directed at mathematically representing the major controlling processes through empirical approaches.

Environmental factors that have not been studied do not present totally new biological problems. The mechanisms by which aquatic organisms adapt to their environment and the changes in biological systems that lead to their breakdown are not different for every possible change in the aquatic environment. Biological studies of the effect of water quality changes should be conducted so as to be useful in explaining how biochemical and physiological responses influence the behavior, survival, reproduction and growth of organisms, and how these in turn influence the success of populations and the stability of communities.

The distribution of heavy metals between soil and soil solution is a key issue in evaluating the environmental impact of long term applications of heavy metals to land. Contamination of soils by heavy metals has been reported by many workers. Metal adsorption is affected by many factors, including soil pH, clay mineralogy, abundance of oxides and organic matter, soil composition and solution ionic strength (Gerrites et al.,1982; McLaren & Crawford,1973; Farrah & Pickering,1976; and Quirk & Posner,1975). The pH is one of the many factors affecting mobility of heavy metals in soils and it is likely to be the most easily managed and the most significant (Jenne,1968).

Contamination of soils, vegetation, surface waters and drainage sediments arising from mining and smelting operations has long been of concern to those undertaking geochemical prospecting for metals. Thornton

(1984) studied the effect of mining and smelting of metals in United Kingdom over a period of several hundred years on the health of plants and animals. He found that there is little impact on them and the economics of farming. He suggests that toxic metals rarely occur alone and their association and interaction with one another and with other components of the environment are known to influence their availability to plants and animals and their ultimate toxicity.

7.0 ADSORPTION OF METALS AT SOLID/SOLUTION INTERFACE

7.1 Introduction

Adsorption from solution is an important process in natural systems, and has also been exploited for use in analytical chemistry and engineering processes. It finds applications in electro-analytical chemistry, ion-exchange, froth flotation, coagulation and collection of trace contaminants. Adsorption reactions are common processes in water and waste water treatment and in the transport of chemical species in the aquatic environment.

7.2 The Solid/Solution Interface

With any solid/water interface there is an associated surface charge and a gradient in electrical potential extending from the interface into the solution phase. The charge originates by non-stoichiometric dissociation of the solid, substitution for an atom in the solid lattice by one of unequal charge, or adsorption of charged species from the solution (Parks,1973). The electrical potential at the surface is fixed by the requirement that at the equilibrium the electrochemical potential of a species must be the same in all phases in any system. Generally, a pair of ions which are present in both the surface phase and in the bulk solution are used to calculate the surface potential and these are called potential determining ions (PDI). For oxide surfaces, OH^- and H^+ are almost always chosen to be the PDI. In any system there is a unique concentration of PDI at which potential determining cations and anions are adsorbed equally. This condition is known as the point of zero charge (PZC). In ideal pure systems the surface charge and surface potential are zero at PZC. For oxides the PZC is usually expressed on a pH scale, so in pure systems when pH < PZC the surface carries a positive charge and when pH > PZC the surface will carry a negative charge. Ions of opposite charge accumulate near the interface and whilst those of like charge are repelled. The potential decays with the distance from the interface and concentration of ions approach their values in the bulk solution. The region, including the surface and the adjacent volume in which ionic concentrations are different from bulk solution, is known as the electrical double layer (EDL).

7.3 Models for Adsorption at the Solid/Solution Interface

It has been long recognized that adsorption of hydrolyzable metal ions on most surfaces is inextricably related to the hydrolysis behavior of the dissolved metal (Leckie & James, 1974). A number of phenomenological models have been proposed to explain the experimental observations, which most often show an abrupt increase in adsorption from nil to almost 100% in a narrow pH range. Adsorption is sometimes accompanied by a reversal of sign of the electrokinetic potential and by rapid coagulation. While the various models differ conceptually, it is difficult to distinguish among them experimentally due to our inability to take measurements and speciation at the solid/solution interface.

7.3.1 Ion-exchange Model

McNaughton and James (1974) proposed that heavy metals are removed from solution by three mechanisms. These include the ion-exchange reaction

$$m(=S\text{-}OH) + M^{x+} \Rightarrow (=S\text{-}O)_mM^{x-m} + mH^+$$

the adsorption and hydrolysis at the surface

$$=S\text{-}OH + mH_2O + M^{x+} \Rightarrow =S\text{-}M(OH)^{x-m}_{x+1} + mH^+$$

and hydrolysis followed by an adsorption reaction

$$M^{x+} + mH_2O \Rightarrow M(OH)_m^{x-m} + mH^+ ;$$

$$M(OH)_m{}^{x-1} + (=S\text{-}OH) \Rightarrow =S\text{-}M(OH)_{m+1}{}^{x-m}$$

where

$=S\text{-}OH$	is the hydrated soil surface
$(=S\text{-}O)_mM^{x-m}$	is the metal ion adsorbed at hydrated the soil surface
$=S\text{-}M(OH)_{m+1}{}^{x-m}$	is the metal hydroxy species adsorbed at the hydrated surface
$M(OH)_m{}^{m-x}$	is the hydroxy metal species

7.3.2 Physical Adsorption Model

The ion-exchange model considers the chemical reactions between surface OH groups and metal ions. This implies that metal ions lose part of their inner hydration sheath and metal ions bind directly with surface hydroxyl groups. This leads to stronger sorption of the more highly charged species and is in contrast with the model of James & Healy (1972).

The critical aspect of the James & Healy model or related adsorption and surface hydrolysis models is that ions are physically adsorbed (they retain their inner hydration sphere and a layer of water separates the adsorbate from the adsorbent). This model treats all the adsorbing species as potential adsorbates, and the extent to which each adsorbed was governed by a combination of coulombic, chemical and solvation terms. The coulombic term could either favor or oppose adsorption depending on the sign of the surface charge. The solvation term expresses the energy required to remove the part of the outer hydration sphere of metal ion and replace it with water of low dielectric constant near the surface. It opposes adsorption and is proportional to the square of the charge of adsorbing species. The third term represented a chemical interaction between the adsorbate and the adsorbent. It favours the adsorption and was used as a fitting parameter in the model. The model predicted that in most cases where the adsorbent was a hydrous oxide, the solvation term was more important than the coulombic term. This implied enhanced adsorption of hydrolyzed lower charged species over that of free aquo ion.

8.0 EXPERIMENTAL METHODS AND MATERIAL

8.1 Analysis of Heavy Metals

The growing realization of the importance of even extremely small amounts of heavy metals in the environment has led to ever-increasing demands for the determination of these metals at trace level concentrations. The levels to be detected range from parts per million to parts per billion. In order to measure at these levels, methods of high sensitivity and selectivity are needed. They must be applicable to all sorts of environmental samples, be accurate and reliable and preferably they should also be convenient and economical. Several methods have been reported in the literature for the analysis of heavy metals they include atomic absorption spectrometry (AAS), X-ray fluorescence spectroscopy, neutron activation analysis and electroanalytical techniques. Each of the above techniques has several advantages and disadvantages in terms of (i) sample size requirement, (ii) sensitivity and detection limit, (iii) form of sample to be analyzed, (iv) complexity of preconcentration techniques, (v) quantitative application, (vi) selectivity, interferences and matrix effects, (vii) number of elements that can be analyzed, (viii) multi element determination, (ix) preparation and use of standards, (x) routine applications, (xi) time, space and the cost Atomic absorption spectroscopy combines high sensitivity, selectivity, simplicity with low cost, routine application and speed of analysis. These factors make it one of the most attractive techniques available to the analytical chemist.

8.2 Atomic Absorption Spectrometry

Atomic absorption depends on the phenomenon whereby atoms of an element are able to absorb electromagnetic radiation which occurs when the toms are unionized and are not bound to similar or other atoms. The sample is initially in solution then sprayed into a flame. At the temperature of flame only a very small fraction of all atoms is excited to emission, 99% remain unexcited. Therefore, the absorption due to a transition from the ground electronic state to a higher energy level is virtually an absolute measure of the number of the atoms in the flame, and hence the concentration of element in a sample. The atoms absorb light at discrete resonant wavelengths which are identical to the light the atom would emit when falling from a higher energy level back to the ground state. The number of atoms capable of absorbing any transmitted light of appropriate wavelength is proportional to the product of the concentration of these atoms in the flame and the length of the light path through the flame. Atomic absorption follows Beer's law namely:

$$\log I/Io = A.B.C$$

where I and Io are the intensities of the light before and after passing through the flame, A is the absorption coefficient, B is the path length of the flame and C is the concentration.

An important advantage of AAS is that it allows measurements of the ratio of two intensities: the intensity of monochromatic light source in the presence and absence of absorbing atoms. The usual procedure for determining the relationship between absorption and atom concentrations in solution is by measuring the absorbance of a number of standard solutions containing a known concentration of the analyte, then drawing a calibration graph by plotting absorbance against concentration. Care should be taken to analyze the unknown solutions within the concentration range of the prepared standards and to ensure the graph is linear at these concentrations.

Nearly all metallic elements of the periodic table can be analyzed by this technique or variation of the procedure. Therefore, the applications are almost unlimited. The only criterion for sample preparation is that the metal should be in solution. The most common solutions are usually of very low pH (<1.0) retaining the metals in solution and also prevent loss due to adsorption on the vessel walls. The technique has been used widely in geochemistry, environmental pollution analysis and water & waste water analysis. Preconcentration techniques for dilute samples are quite easy to use, they include ion-exchange and solvent extraction.

Interferences associated with this technique that have been recognized are (i) spectral, (ii) matrix, (iii) molecular and (iv) chemical:

i) Spectral: this type of interference is caused by the light source radiating spectral lines which are not resolved by the monochromator.

ii) Matrix: this is caused by a variation in solution viscosity between sample and standards. Interference can be removed by using standard addition methods, matching the matrix of both standard and sample or by removing the analyte completely from the matrix by solvent extraction or ion-exchange.

iii) Molecular: all complex solutions containing many different elements give absorption bands caused by molecular species. The major element causing such interferences is calcium which blocks or absorbs some of the light of the light passing through the flame. The species are usually hydroxides or halides bounded to the major metal.

iv) Chemical: this is the most common interference encountered in AAS. Depending on the analyte element, different flame temperatures are required for analysis. Some elements form very soluble oxides e.g. chromium, and a high temperature flame such as acetylene-nitrous oxide is needed to break down the oxide. The stoichiometry of the flame (oxidizing or reducing) will overcome some chemical interferences by preventing the formation of a stable oxide. Other elements, however, due to the flame temperature may be ionized, preventing absorption. This effect can be reduced by the addition in excess of a more easily ionized element than the analyte, usually sodium or potassium.

Interferences may cause enhancement or depression of the analyte signal and so great care is necessary to ensure that standards resemble the unknown solutions as clearly as possible. However, because the initial solution may be complex in nature, such a process is difficult to achieve and the standard addition is the only viable method for overcoming these difficulties.

8.3 Sampling and Treatment of Samples

Soil was collected from Northfield Brook in Oxfordshire, which is a fairly uncontaminated site,where metal input-rate history is maintained by MAFF. The soil samples were collected in a plastic bag and transported to the laboratory. The samples were dried in an oven at 100° C for 24h. Large lumps and rocky granules were removed and the remainder sieved to a particle size of less than 80 mesh (110 µm). Specific surface area was found (by BET nitrogen adsorption technique) to be 4.2 m^2/g.

8.3.1 Digestion of Samples

1g of soil was taken into an Erlenmeyer flask and 10ml of one of the acid solutions was added. The flask was heated on a hot plate at 95°C for the appropriate time periods. The sample was filtered through Whatman filter paper (No.41) and the volume was made up to 50ml in a volumetric flask and then analyzed by AAS (The program of analysis is given in Table 1).

8.4 Static Adsorption System

1g of soil was taken into an Erlenmeyer flask and 10 ml of test solution of known metal / metals concentration was added. The flask was covered to avoid any contamination and left on a mechanical shaker (100 strokes per

Table 1
The Programme of the Analysis

Extractant Composition	No. of replicates Analysis	Digestion time (hours)
HNO_3:HCl		
1:3	3	2
1:3	3	3
1:3	3	4
1:2	3	2
1:2	3	3
1:2	3	4
1:1	3	2
1:1	3	3
1:1	3	4
HNO_3:H_2SO_4		
1:3	3	2
1:3	3	3
1:3	3	4
1:2	3	2
1:2	3	3
1:2	3	4
1:1	3	2
1:1	3	3
1:1	3	4

minutes) for different time periods (pH of the system was adjusted to 6.5). Subsequently, the solid and liquid phases were separated through Whatman filter paper (No.41). Each phase was digested/treated and diluted with distilled water . Aqueous sample was taken into an Erlenmeyer flask and 10 ml of one of the acid solution was added. The flask was heated on a hot plate at 95°C for 90 minutes and stored in an acid washed glass bottle. (Metal uptake was calculated from the aqueous phase, and results were randomly checked by analyzing solid phase, after adjusting the background levels).

8.5 Dynamic Adsorption System

15 g of soil/silt was packed in a glass column which was connected with a reservoir containing a test solution of known metal/metals concentration (pH value of the system was adjusted to 6.5). The flow of solution was adjusted by means of a restrictor. The test solution was passed through the column and the effluent were collected after various intervals of time (the flow rate was adjusted to 1 ml/ 1.25 min.) (Setting of the apparatus is shown in Fig.4).

8.6 pH Variation Modes

5g of sample was taken into an Erlenmeyer flask and 50 ml of pH

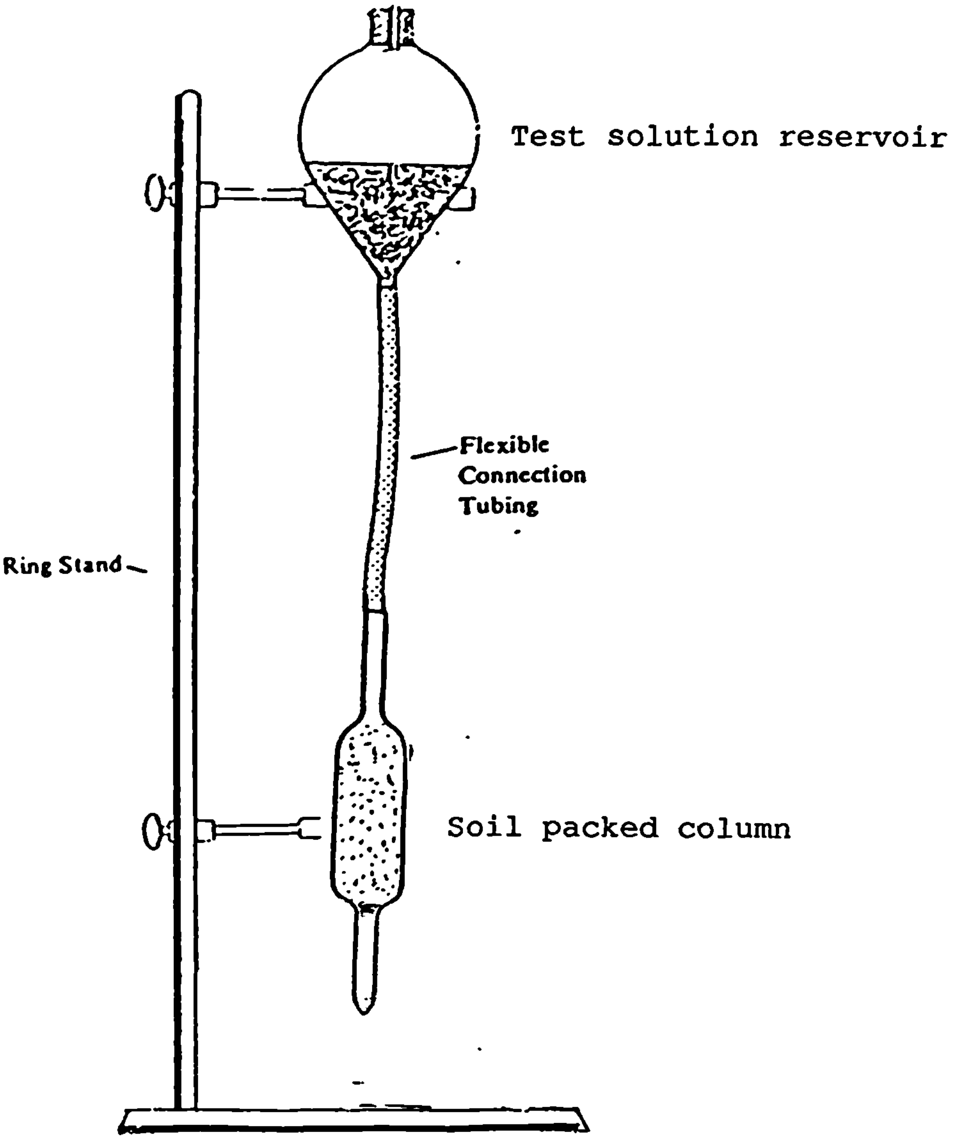


Figure Setting of the apparatus usede in dynamic adsorption system adjusted test solution (200 ppm) was added (pH was adjusted by the addition of HNO_3-NaOH). The flask was covered to avoid any contamination and left on a mechanical shaker (100 strokes per min.) for 15 minutes. The solid and liquid phases were separated and digested/treated followed by dilution with distilled water.

8.7 Analysis

All samples were analyzed using a Perkin Elmer 2380 Model Atomic Absorption Spectrophotometer equipped with printer according to manufacturer's operating conditions.

8.8 Surface Loading

2g of soil sample was taken into a flask and 20 ml of the concentrated test solution was added and the flask was kept covered for 24h and then the solid & liquid phases were separated, and the soil was dried in an oven at 95°C for 36h.

8.9 Reagents

All reagents used in this study were analytical grade. Water was distilled deionized. Approximately 1.0M and 0.1M nitric acid were prepared by diluting concentrated redistilled nitric acid. Carbonate free sodium hydroxide was stored in a rubber-capped bottle. Stock solutions of metals were obtained from BDH. Acid solutions used were also AGR [(HNO_3 70% W/W) (HCL 36% W/W)].

8.10 Synthesis of Sea-water

Sea-water was synthesized by adding 0.999 g $CaCO_3$, 2.074 g MgO, 1.414 g K_2CO_3 and 25.41 g NaCl to a 1-liter flask, dissolving in a minimum volume of 1:1 HCl and diluted to the volume with distilled water. The final solution gave the values of :

Na	10000	ppm
Mg	1250	ppm
Ca	400	ppm
K	400	ppm

8.11 Oxidation of Organic Contents

1g of soil was taken into a flask and 20 ml of H_2O_2 was addded and the flask was left covered for 24h then the both phases were separated and the soil was dried in an oven at 95°C for 36h.

9.0 Results and Discussion

9.1 Adsorption Isotherms

Adsorption isotherms describe the partitioning of a chemical species between adsorbed and dissolved phases. Isotherms are often displayed graphically as plots of adsorption density (Γ) versus equilibrium concentration of adsorbate (C_{eq}). Often, an equilibrium constant is defined relating adsorption density to equilibrium concentration of adsorbate, implicitly assuming that activity coefficients in solution and on the surface are constant for the conditions of the experiment. In addition there is often an unstated assumption that chemical speciation is unimportant or remains the same.

9.1.1 The Langmuir Isotherm

The Langmuir isotherm derives from the assumption that the free energy of adsorption is independent of surface coverage. That is the driving force for adsorption onto an adsorbate free surface is the same for adsorption onto nearly filled surface. For gas, this assumption is often taken to mean that adsorbed molecules do not interact with one another at all. For adsorption from solution, a more acceptable model is that of an ideal surface solution, in which the interaction between adjacent surface species are equivalent. That is, the affinity of the adsorbate for a given site is independent of whether the neighboring sites are occupied by water or adsorbate species.

The Langmuir equation is usually expressed as follows:

$$\frac{C}{x/m} = \frac{1}{K_1 K_2} + \frac{C}{K_2}$$

where

C = equilibrium concentration of adsorbate

x/m = amount of adsorbate adsorbed per unit of adsorbent

K_2 = adsorption maximum

K_1 = a constant related to the bonding energy of the adsorbent to the adsorbate

This equation was originally derived by Langmuir to illustrate that gas molecules are adsorbed to a solid surface as a monolayer with a constant and specific energy of adsorption; it has been since applied to study the adsorptive behavior of ions to any solid surface (Reddy & Perkins, 1973).

Linearity of a plot of $C/(\dot{x}/m)$ vs C_{eq} implies that the adsorbent will adsorb only a given amount of the ion and that this will be as monolayer with a uniform bonding energy. A curved relationship can be interpreted to imply that the adsorbent will adsorb a small amount with constant and firm bond energy, a slightly greater amount less firmly and so on. In this study, the equation has allowed the determination of the adsorption maxima for copper, lead and zinc.

9.1.2 Experimental Results

Adsorption isotherms provide a means of evaluating the capacity of soils to adsorb heavy metals. The Langmuir adsorption isotherm has been used to describe the relationship between the adsorption of ions by a solid and the concentration of the ion in solution (Boyd et al.,1947). McLellan and Pock (1988) found that performing batch tests, specifically isotherms studies, can show the performance of a peat for removal of specific metal ions.

In general, increasing ionic strength reduced adsorption of most of the metals. Increasing concentration of competing ions may result in reducing the activity of the particular element. The data for Pb, Cu and Zn adsorption by soils were applied to the linearised form of Langmuir equation and the results are shown in Tables 2 and 3. The maximum adsorption capacity of adsorbent for adsorbate in various systems is [calculated from the adsorption isotherms of Cu, Pb and Zn (Figures 9.01, 9.02, and 9.03)] shown in Table 3. The value of Γ (Adsorption density, amount of adsorbate adsorbed on per unit mass of adsorbent) increases in the following order:

$$Pb < Cu < Zn \quad .... \quad 9.1$$

which shows that adsorption behaviour of Cu and Zn is very much similar in terms of maximum adsorption capacity (Γ_{Cu} 17.7 µmole/g ; Γ_{Zn} 14.3 µmole/g and Γ_{Pb} 8.29 µmole/g) it may also indicate that number of sites available are same at least for Cu and Zn.

Table 2. Pb, Cu and Zn adsorption onto soils (20 ml + 2g)

Metal Conc. (ppm) added	C_{eq} (ppm)	C/x/m
Lead		
10	0.01	0.00005
25	0.30	0.0006
50	1.20	0.0012
75	4.30	0.0030
100	16.70	0.01
Copper		
10	1.20	0.00681
25	3.30	0.00760
50	11.90	0.01561
75	25.50	0.02570
100	50.00	0.05000
Zinc		
10	1.20	0.00681
25	3.30	0.00760
50	11.90	0.01561
75	25.60	0.02570
100	59.90	0.07468

Table 3. Maximum adsorption capacity of adsorbent for adsorbates.

Metal	Maximum Adsorption Capacity
Lead	1719 µg/g/
Copper	1128 µg/g
Zinc	938 µg/g

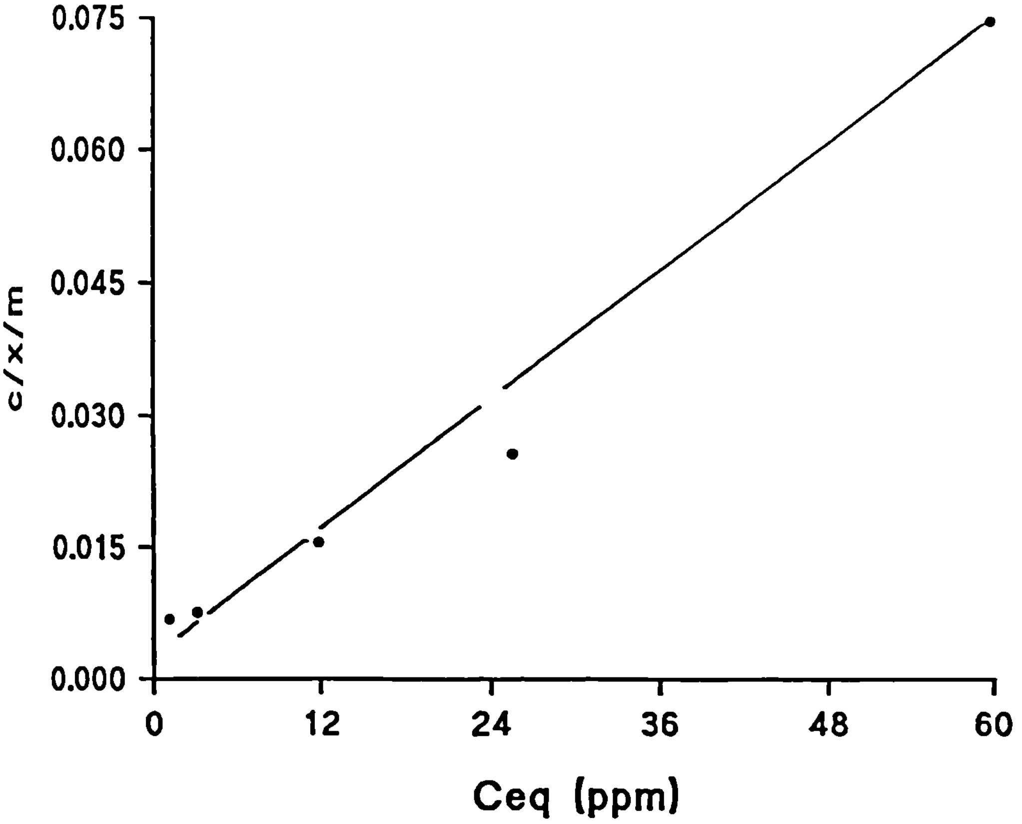


Figure A-1
Adsorption isotherm for Zn adsorbing onto soils

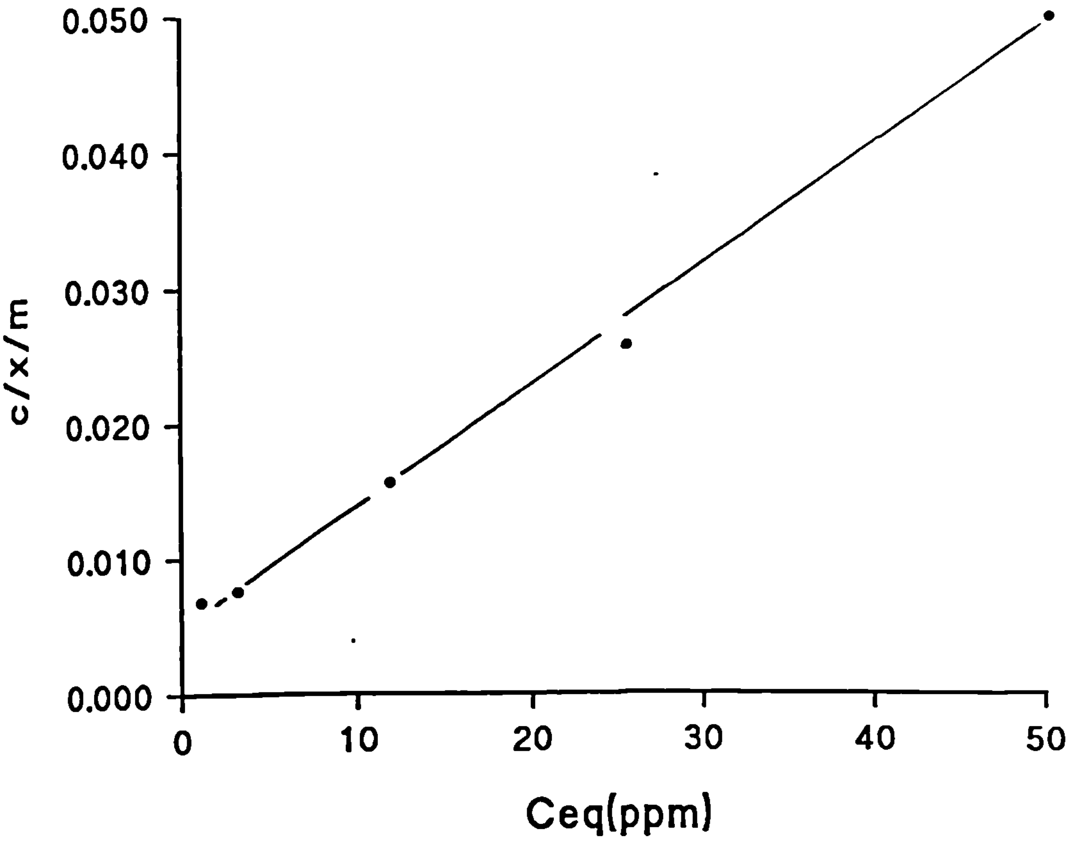


Figure A-2
Adsorption isotherm for Cu adsorbing onto soils

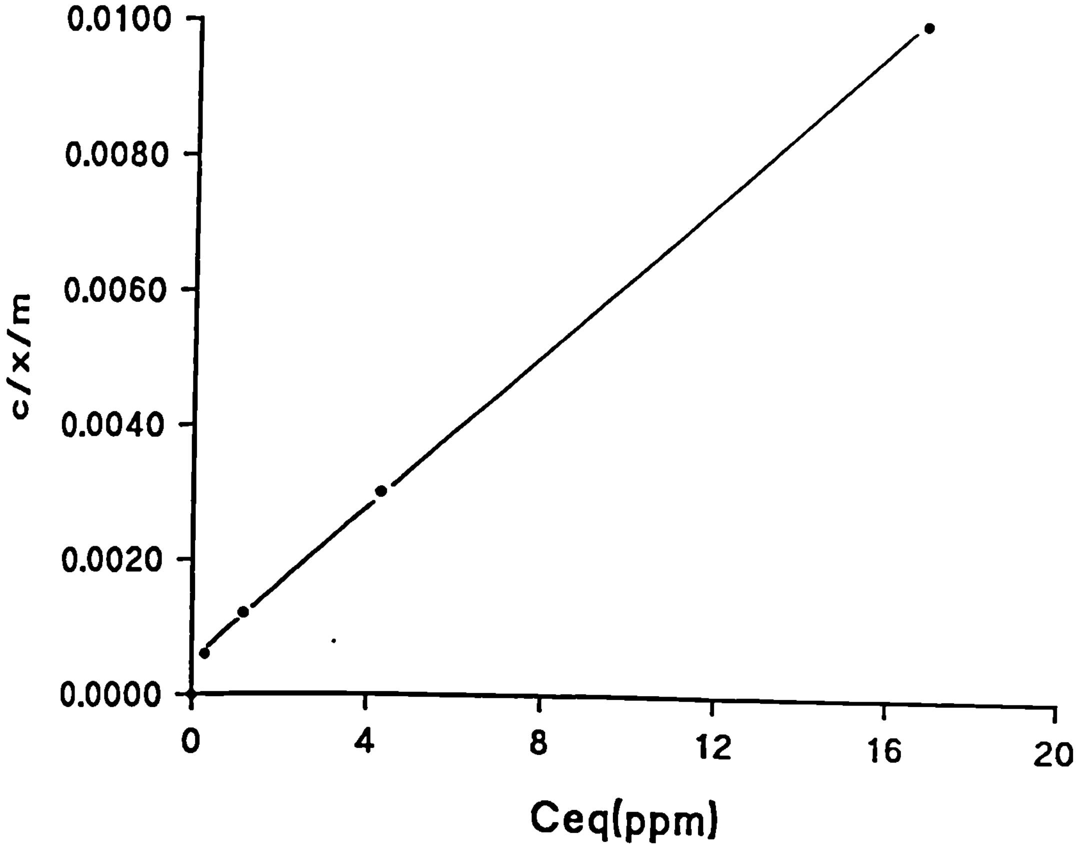


Figure A-3
Adsorption isotherm for Pb adsorbing onto soils

9.2 Adsorption of Metals onto Soils as Function of pH

The adsorption of Cu(II), Cd(II), Pb(II) & Zn(II) as function of pH onto soils is shown in Figures 9.04-9.07 where percent adsorbed refers to the fraction of total metal removed from the solution phase. Adsorption edges for Pb(II), Cu(II), Zn(II) and Cd(II) are in the range of 3.5-5.5, 3-6.5, 5.5-7.5 and 6-8 respectively. It is also observed that the pH of the abrupt adsorption increases in the order of:

$$Pb(II) < Cu(II) < Zn(II) < Cd(II) \;\ldots\ldots\; (9.2)$$

Figures 9.04-9.07 show the removal of Cd, Cu, Pb & Zn from their solution as a function of pH. The fraction adsorbed increases from 5% to 90% for Cu, 3% to 82% for Cd, 5% to 86% for Pb and 5% to 80% for Zn in the pH range of 3-6.5, 6-8, 3.5-5.5 and 5.5-7.5 respectively. The adsorption behaviour of metals as function of pH shows that the amount adsorbed increases with increasing pH. An increase in negative surface charge, as pH increases (as oxide surfaces are charged through reactions with $OH^-$and H^+ in solutions. These reactions are of type:

$$\underline{X}OH + H_2O \;\ldots\ldots\ldots\ldots\; \underline{X}O^- + H_3O^+$$

$$\underline{X}OH + H_2O \;\ldots\ldots\ldots\ldots\; \underline{X}OH^+_2 + OH^-$$

where underlining indicates the solid phase, $\underline{X}OH$ represents the hydrated

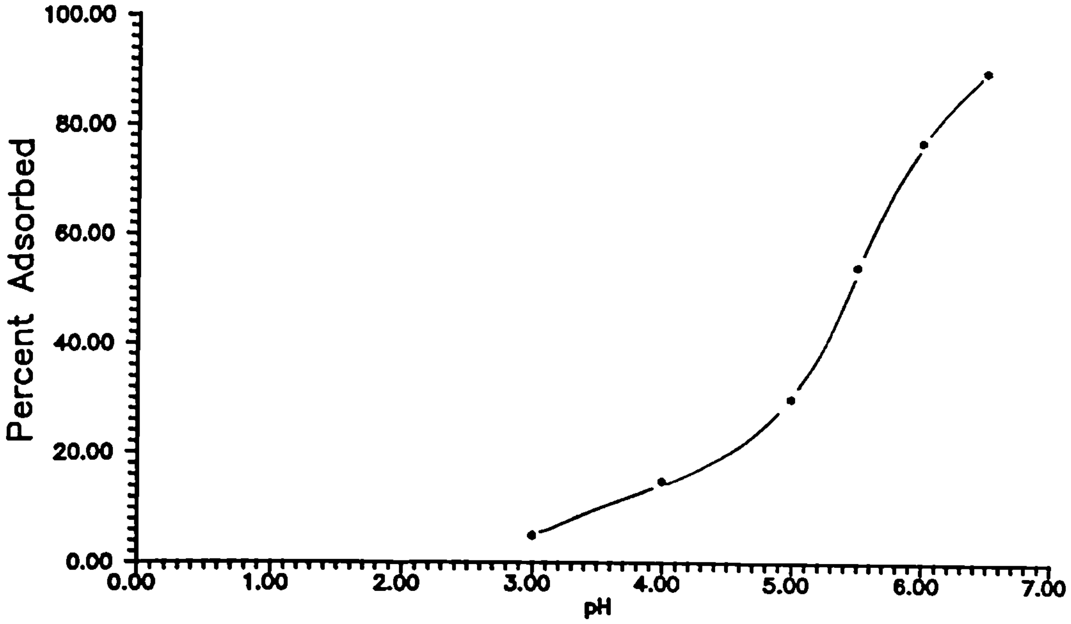


Figure 9·04
Adsorption of Cu onto soils as function of pH
Cu(200 ppm)10 ml/g

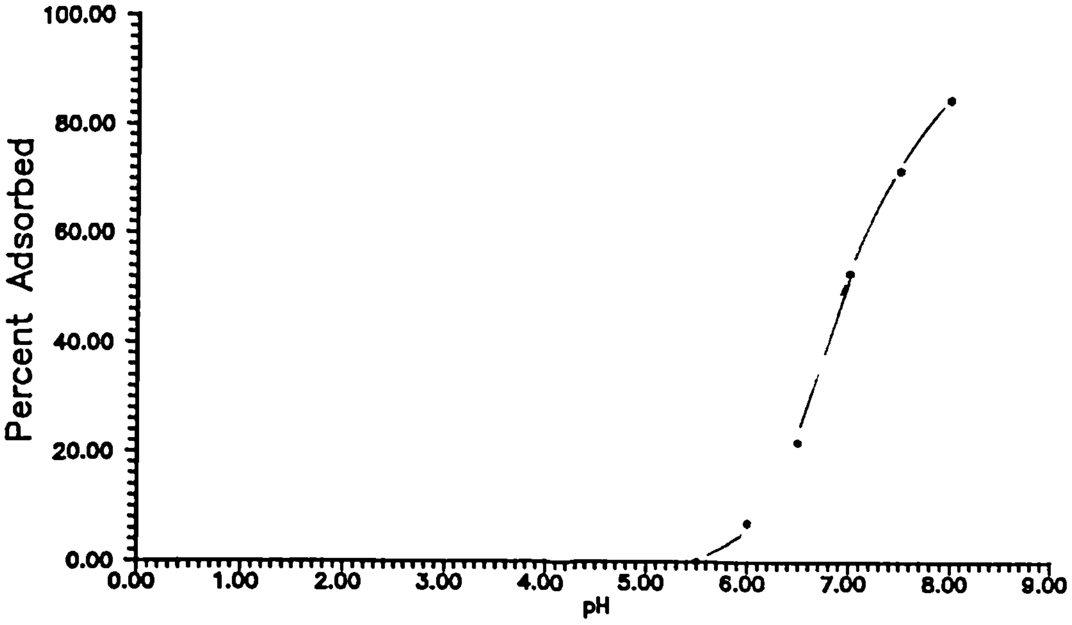


Figure 9 05
Adsorption of Cd onto soils as function of pH
Cd(200 ppm)10 ml/g

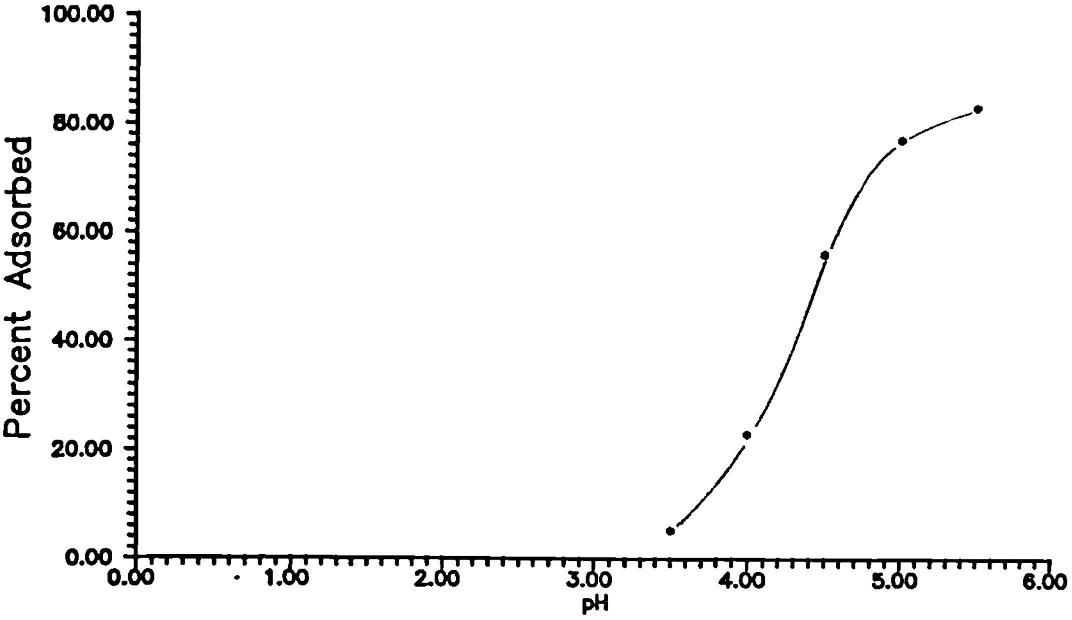


Figure 9·06
Adsorption of Pb onto soils as function of pH
Pb(200 ppm)10 ml/g

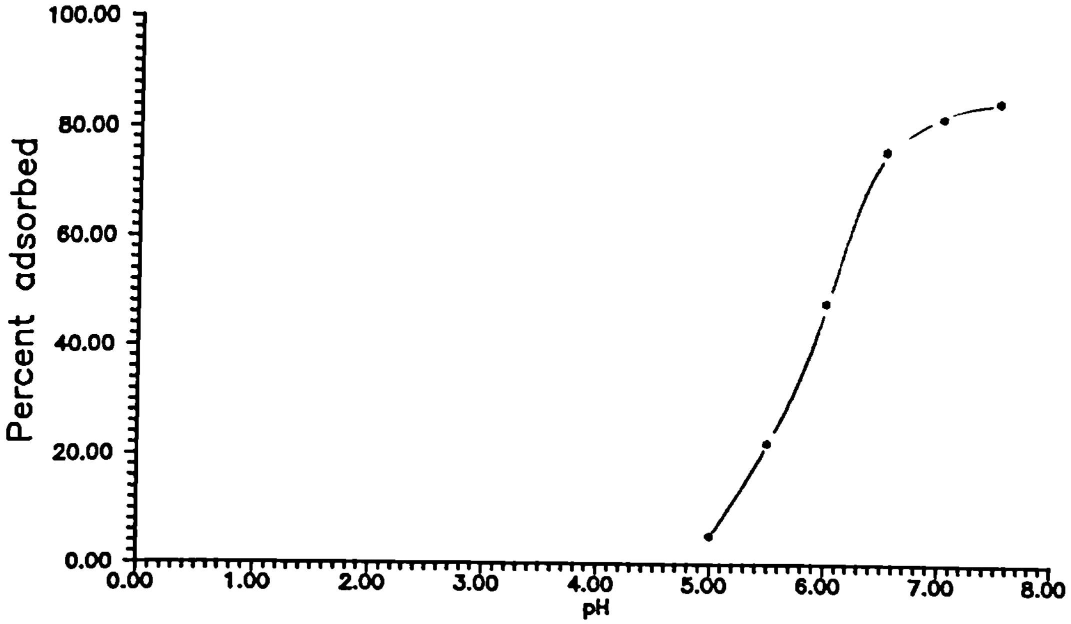


Figure 9.07
Adsorption of Zn onto soils as function of pH
Zn(200 ppm)10 ml/g

surface and X is the central metal atom of the oxide (Si in SiO_2). In any system there is a unique concentration of PDI at which potential determining cations and anions are adsorbed equally. This condition is known as the point of zero charge (PZC). In ideal pure systems the surface charge and surface potential are zero at PZC. For oxides the PZC is usually expressed on a pH scale, so in pure systems when pH < PZC the surface carries a positive charge and when pH > PZC the surface will carry a negative charge). It reflects a corresponding increase in the availability of adsorption sites. This result, along with less competition for H^+, could cause the increase of heavy metals adsorption onto soils at high pH. In addition, Farrah & Pickering (1976) suggested that increasing the pH the solution will expose new sites of the soils (e.g. expansion by hydroxyl ion adsorption).

The pH, and the nature of heavy metal species i.e. their charge and hydration, also influence the sorption. As the pH increases the hydrolysis products of the dissolved metal ions begin to appear in solution, decreasing the average charge on the ion. Changing the pH of copper solution from the value of 3.5 to the value of 6.5 played a significant role in copper adsorption. A sharp increase in copper removal occured when the copper solution pH's changed. Species distribution diagrams presented by Mesmer and Baes (1974) showed that a hydrolysis of Cu ions to $Cu(OH)^+$ became significant at pH values above 4.0, followed by Cu^{+2}, this can account for the sharp increase in adsorption of Cu, as Cu^{+2} requires two surface sites while $Cu(OH)^+$ needs one site so

$Cu(OH)^+$ is preferential adsoption species. At pH 6.5 relative concentration of Cu^{+2} decreases, but the importance of $Cu(OH)_2$ increases and it becomes dominant above pH 7.0. Zinc removal increased with increasing pH up to 7.5, where $Zn(OH)^+$ became dominant mechanism for Zn removal. The data indicates that lead adsorption also increases with increasing the pH from 3.5 to 5.5. Below pH 6.0 most of the lead is present in the form of Pb^{+2}, and above that pH it is hydrolyzed to $Pb(OH)^+$ and $Pb(OH)_2$. The inorganic speciation of cadmium in water has similarities to that of lead, but is simpler in that the free cation (hydrated) exists to relatively high pH values, i.e. < 7 to 8, below which the Cd^{+2} occurs. This indicates that metals speciation in solution is dominated by hydroxy- complexes for the pH range of their adsorption edges.

Heavy metal ions distinguish themselves from alkali and alkaline earth ions in solution by undergoing hydrolysis at lower pH values and by displaying multiple hydrolysis at pH values encountered in the environment. It is likely that adsorbed $M\ (OH)^+$ is the predominant metal surface species, since it has been shown that adsorption of metal ions on various oxide surfaces increases abruptly in the pH range where hydrolysis products become a significant fraction of the dissolved metal (Leckie & Davis, 1978) & Table 4. This implies that the $M(OH)^+$ species plays an important role in metal ion adsorption. While there may be a general trend governing the order of pH value at the abrupt adsorption, it is premature to draw an unified theory. The log values of various metal hydroxy species equilibrium constants are listed in table 5 (Patterson &

Table 4.
The Speciation of Aqueous Metal Ions (Huang et al.,1986)

Metal	Speciation at pH of abrupt adsorption
Lead	$Pb(OH)^+$ Pb^{+2}
Copper	$Cu(OH)^+$
Zinc	$Zn(OH)^+$ Zn^{+2}
Cadmium	$Cd(OH)^+$ $Cd(OH)_2$

Table.5.
Log of Equilibrium Constant Values of Various of Metal Hydroxy Species (Patterson & Passino, 1987 Cit Zabowski et al., 1987)

Equilibria	Cd	Co	Cu	Hg	Ni	Pb	Zn
$M^{2+} + OH^- = MOH^+$	4.27	4.30	6.30	10.9	4.10	6.67	5.0
$M^{2+} + 2OH^- = M(OH)_2$	8.26	8.40	13.6	22.3	8.0	11.4	11
$M^{2+} + 3OH^- = M(OH)_3^{-1}$	8.61	9.70	15.3	21.4	11.0	14.6	13.
$M^{2+} + 4OH^- = M(OH)_4^{-2}$	9.07	10.2	16.4	-	-	-	14.

Passino, 1987) which shows that the value of equilibrium constant of the first hydrolysis species of various metals increases in the following order:

$$Pb < Cu < Zn < Cd \quad ..... \quad (9.3)$$

which is similar to the series 9.2.

The observed uptake of hydrolyzable metal ions onto oxides and/or other mineral surfaces may be summarized as follows:

(I) Uptake is strongly pH dependent and usually occurs over a narrow pH range (two to three unit wide).

(II) Fractional adsorption decreases with increasing total metal concentration.

(III) The shape of fractional adsorption -pH curve shows that OH^- is consumed or H^+ is released as adsorption increases.

(IV) The location of the adsorption region on the pH scale is characteristic of a particular metal ion.

Most of the metals displayed similar behaviour at lower pH values. There was an increase in metal solubility and, as a result, a decrease in metal retention. This is alarming, since any acidic wastes, such as wastes associated with battery recycling and similar operations, could be potentially dangerous to groundwater because of the transport of excess lead to the shallow groundwater zone (Kotuby-Amacher & Gambrell,1988). At higher pH values there was a decrease in metal solubility and an increase in metal retention. These results imply that metals removal by soils were accomplished by two processes. The first process was by precipitation of metal due to pH increase. The second process was adsorption of metal onto the soils (Inskeep & Bahan,1983). The effect of pH is related to its great influence on the charge and structure of the adsorbing surfaces and on the ionic composition of the soil solution (Abd-Elfatah & Wada,1981).

At higher pH values insoluble oxides of Fe and Mn tend to adsorb heavy metals onto their surfaces and these oxides become soluble at lower pH values resulting the release of metals into the solution. The pH values dominate in the adsorption process of metals onto clay minerals. Heavy metals may be completely released under extreme acidic conditions. Two important properties of the clay mineral are that they generally have a net negative charge which attracts H^+ ions and present a large surface area per unit weight for further chemical reactions. The weathering rate of minerals is increased by increasing temperature and acidity. Increasing H^+ concentration not only increases the replacement of metal ions in the lattice but may also create conditions for dissolution of less soluble ions, like those of aluminum, which are very common components of lattices. Al^{+3} is soluble below pH 4.5 and hence its concentration in drainage waters has been increased through the lower pH of rain acidified by the reactions of SO_4, CO_2, and NO_x.

A comparison of various nitric and hydrochloric acid mixtures for the determination of metal back-ground levels in soil samples is shown in Table 6. For most metal extraction with nitric and hydrochloric acid mixture(1:1) was not very effective while (1:2) and (1:3) gave the higher results (because of the higher solubility of Cl^- and NO_3^- species). It was also observed that the extraction of metals from clays with the acid mixture of nitric acid and sulphuric acid mixtures was not very effective and the lowest results were recorded. It may be because of the formation of insoluble sulphides. Calcium and magnesium are the common constituents of soil which may cause the lower extraction of metals as the results of the precipitation of calcium and magnesium sulphides.

Agricultural soils have been the recipient of large inputs of toxic materials from the addition of pesticides and contaminated fertilizers. Some of this material has a rather short-time in the soil due to the leaching, volatilization or uptake by plants. However, a substantial amount remains stored in the soils. This may be specially true for heavy metals and organic pesticides, that are present in the soils as insoluble products or adsorbed on the surfaces of soil substrate. The most important question regarding these stored toxic materials is the potential in the future for increased mobility resulting in their leaching into ground waters or uptake by edible plants. These metals are highly mobilized

Table 6. Extraction of Metals from the Soils (Back-ground metal levels)

Extractant Composition	Digestion Time (hrs)	Cd ppm	Cr ppm	Cu ppm	Pb ppm	Zn ppm
HNO_3: HCl						
1:1	2	0	8	22	9	47
1:1	3	0	8	22	9	48
1:1	4	0	8	22	10	48
1:2	2	0	8	23	11	48
1:2	3	0	9	24	11	49
1:2	4	0	9	25	12	50
1:3	2	0	8	22	11	49
1:3	3	0	9	24	12	50
1:3	4	1	9	24	12	50
HNO_3: H_2SO_4						
1:1	2	0	6	20	8	47
1:1	3	0	6	20	9	47
1:1	4	0	6	20	9	47
1:2	2	0	6	20	8	48
1:2	3	0	7	20	9	48
1:2	4	0	7	21	9	48
1:3	4	0	7	22	9	48

under the acidic conditions because of the competition with H^+. Having established acidification as a major determinant of the mobility of heavy metals and other contaminants in contaminated soils, it is necessary to review the possibility in the future for broad-scale changes in the acid status of agricultural soils. On a regional scale, the most important source of acidity could be the acid deposition from the combustion of fossil fuels or the acid drainage from mining activities. In addition to acid deposition, high inputs of nitrogen fertilizer and removal of crops could be the major sources of acidification. Addition of the fertilizer results in the production of H^+ in soils after nitrification and crops removal may result in a loss of base cations from the soils which may decrease its acid neutralization capacity. These soils could be protected from acidification by the routine practices of liming which may help to maintain the soils structural stability and raise the soil's pH value to near 6. John et al.,(1972) and Muller et al.,(1976) found that lowering the soil pH was associated with increasing concentration of certain heavy metals in radish and soybeans. Wallace et at.,(1977) have observed decreased cadmium uptake by certain plants with the addition of lime to the soil. Perhaps a new source of soil acidification in Europe may occur if current plans to cut back agricultural production in EC countries are implemented. Serious discussions are underway to reduce, by a large fraction, the area currently engaged in agricultural activities. One result could be the abandoning of farm-lands on a large scale. If these land are no longer limed there might be a large and rapid increase in soil acidity. This effect will be aggravated in areas receiving high levels of acid depositions. Because some of these soils have been the recipient of cumulative doses of heavy metals over several decades the sudden decline in pH may cause large discharges of metal into ground and surface waters.

9.3 Adsorption of Metals onto Soils as Function of Time

Fractional adsorption of Cu, Cd, Ni, Pb & Zn ions is shown in Figures 9.08-9.16 where percent adsorbed refers to the fraction of total metal removed from the solution phase as a function of time onto soils. To determine the equilibrium contact time 10 ml portions of standard stock solutions of the metals were placed in 20 ml flasks each containing 1g of soil. The sample were placed on a mechanical shaker for different time periods (5, 10, 15, 20 and 30 minutes). At the end of each period, the samples were treated and the metal concentrations were determined in the aqueous phase.

Results showed the sorption reactions were almost completed in 15 to 30 minutes. These results were in agreement with Christensen (1984) and Steel et al.,(1977) who found that most metals (2g/20 ml) reached near equilibrium within 30 minutes. Sidle & Kardos (1977) obtained results with a forest soil with 3 to 30 hours equilibrium times at low adsorbent concentration (5g/50 ml). Equilibrium of various metals (1g/10 ml) on SiO_2 surfaces was found to be nearly completed in 5-10 minutes by Vuceta (1978).

Until recently, laboratory studies of metal sorption have focused on equilibrium description of metal-particle interactions. Now, however, there is a growing body of literature describing kinetics studies of metal ion adsorption. Most studies of heavy metals adsorption onto oxides or clays have been

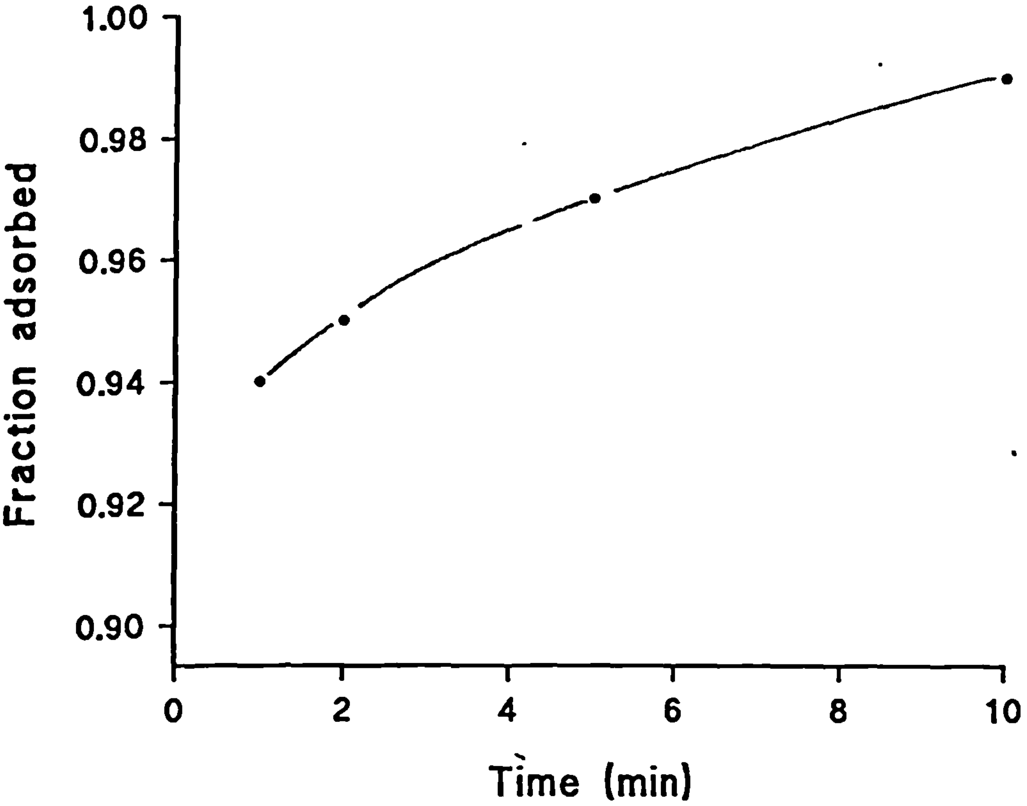


Figure 9.08
Adsorption of Cu onto soils as function of time
Cu(10 ppm)10 ml/g

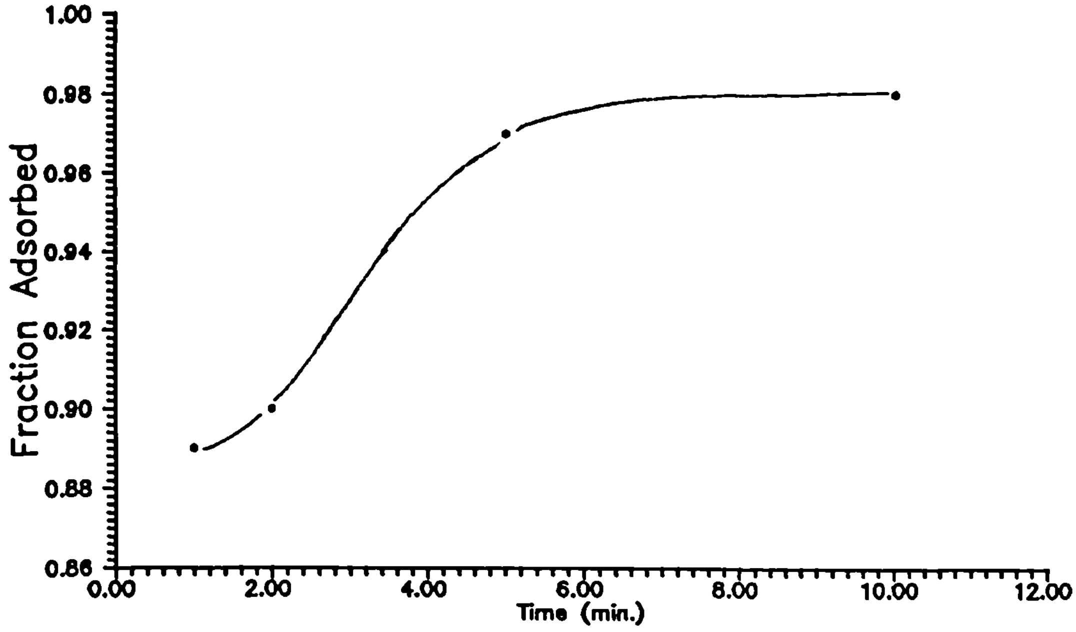


Figure 9.09
Adsorption of Cu onto soils as function of time
Cu(50 ppm)10 ml/g

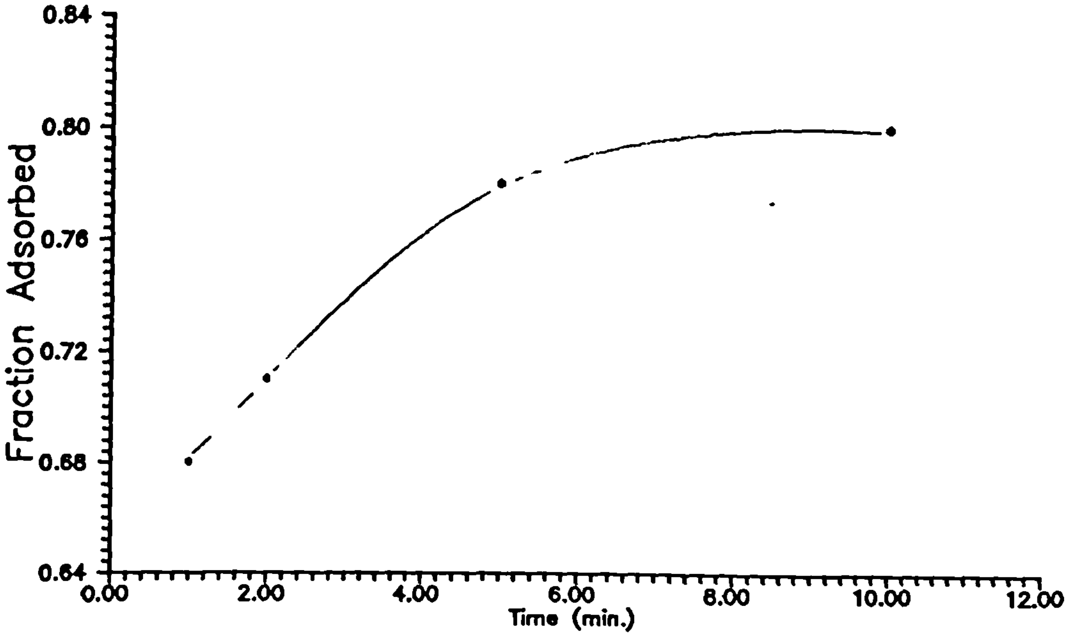


Figure 9.10
Adsorption of Cu onto soils as function of time
Cu(100 ppm)10 ml/g

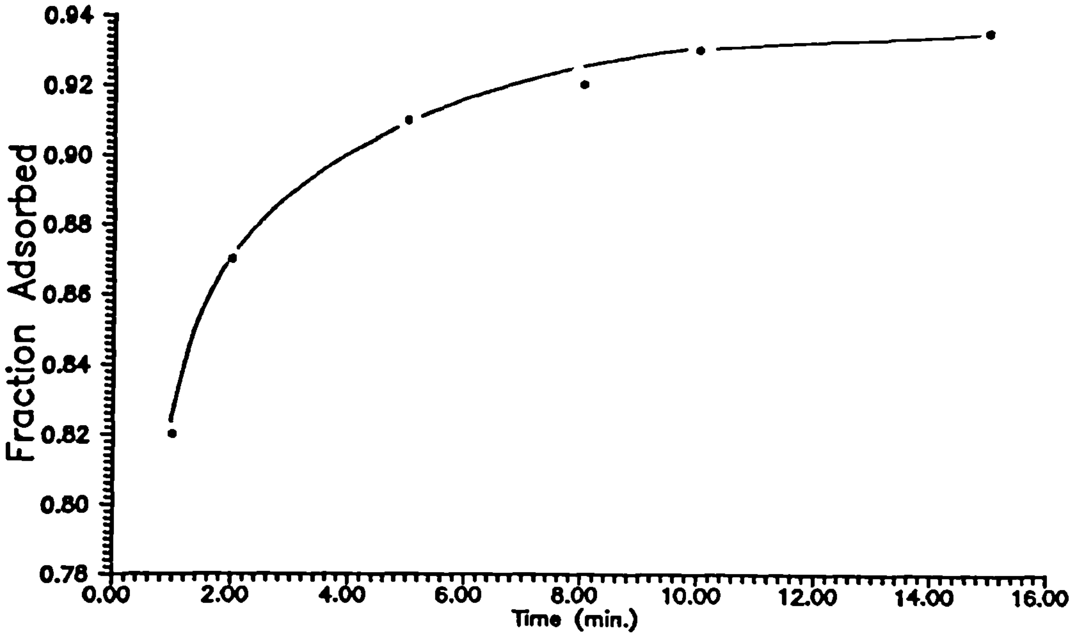


Figure 9.11
Adsorption of Zn onto soils as function of time
Zn(10 ppm)10 ml/g

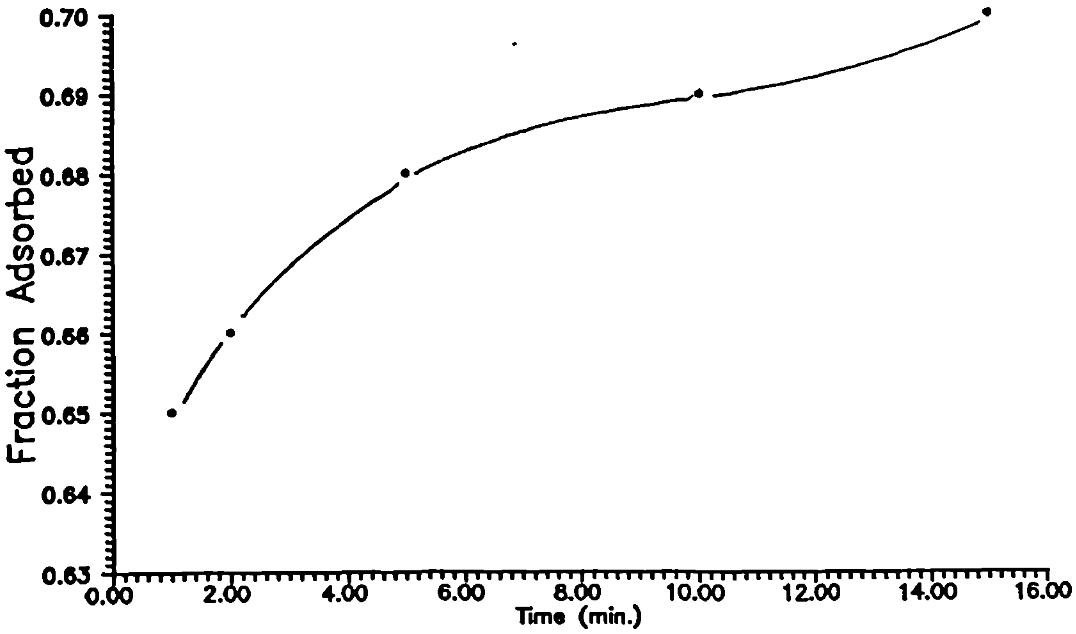


Figure 9.1·2
Adsorption of Zn onto soils as function of time
Zn(100 ppm)10 ml/g

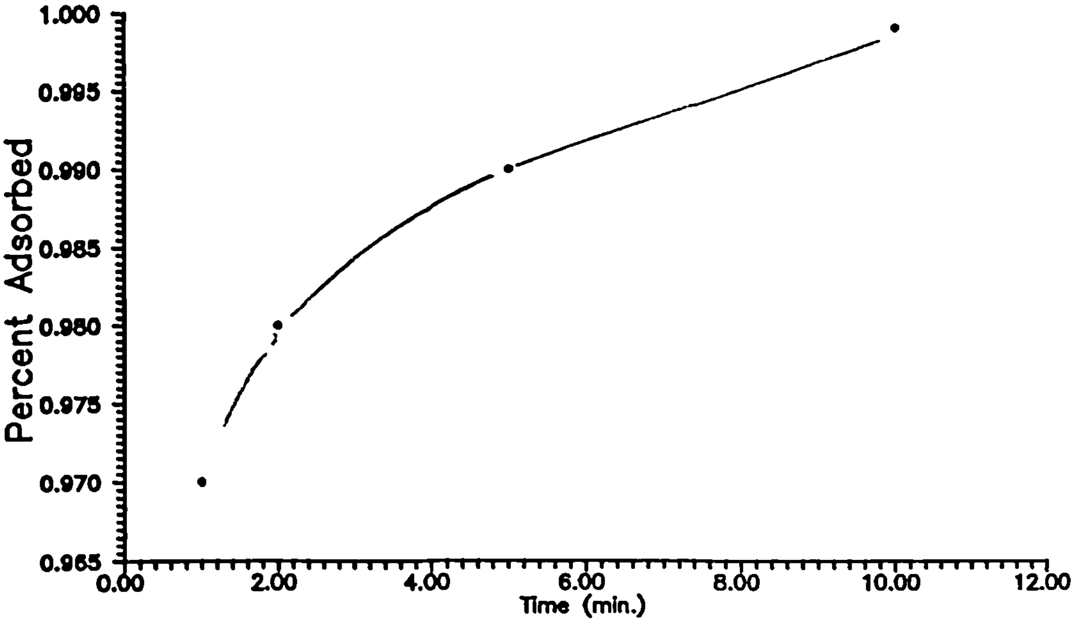


Figure 9.13
Adsorption of Pb onto soils as function of time
Pb(100 ppm)10 ml/g

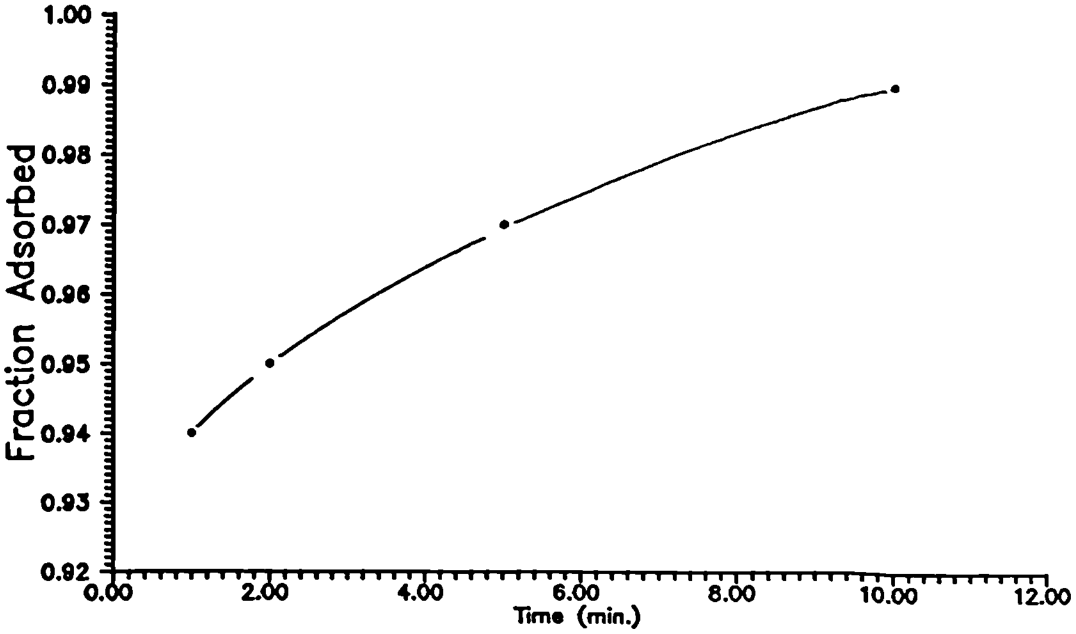


Figure 9.14
Adsorption of Pb onto soils as function of time
Pb(20 ppm)10 ml/g

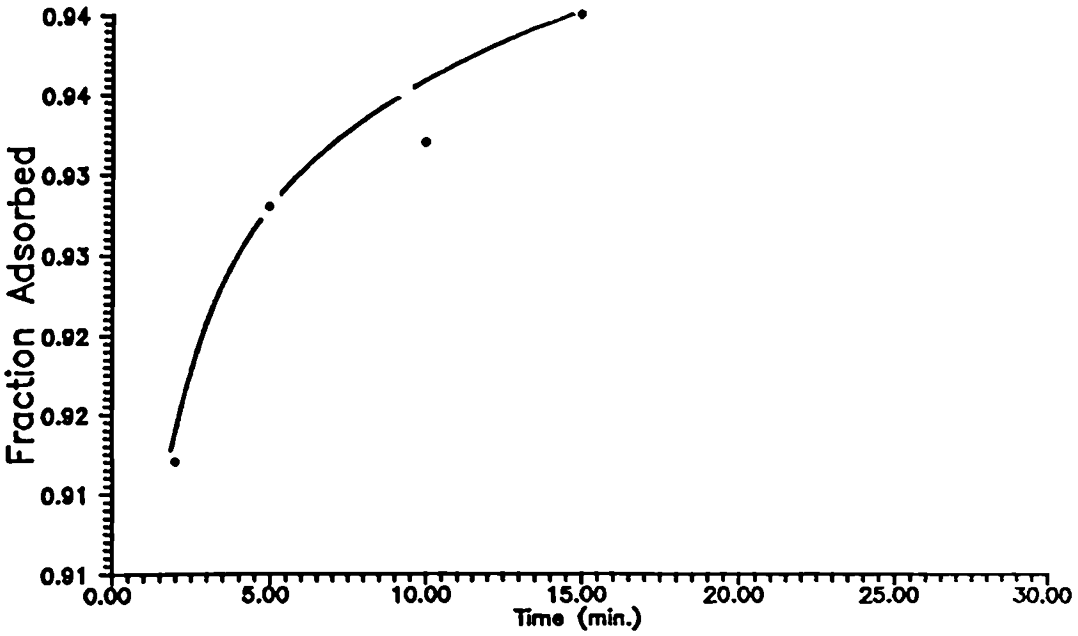


Figure 9.15
Adsorption of Cd onto soils as function of time
Cd(10 ppm)10 ml/g

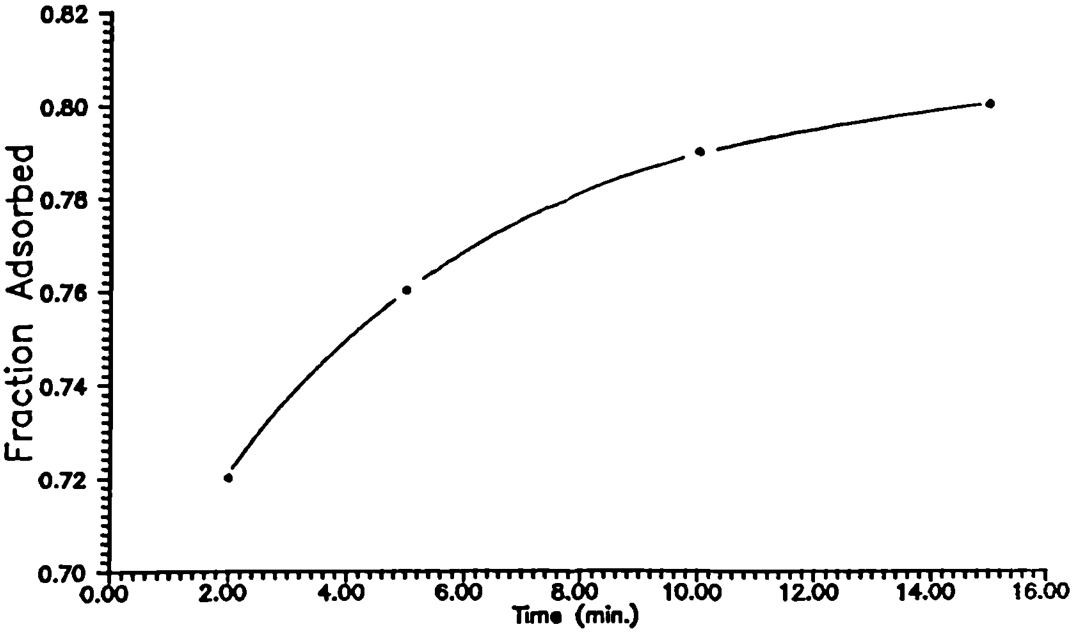


Figure 9.16
Adsorption of Ni onto soils as function of time
Ni(10 ppm)10 ml/g

characterized either by a rapid attainment of equilibrium or by two-step kinetics. In the latter case the first step is rapid, being complete within a few minutes and is attributed to adsorption onto easily accessible surface sites (the maximum adsorption density of copper, lead and zinc, adsorbing onto soils, is shown in Table 3 which reflects that the number of adsorption sites that could be available to metal ions is far higher than they are as shown in Table 7). The second step is much slower often continuing for hours, even days and is related to solid state diffusion of adsorbate into the bulk adsorbent (Yates,1975).

It is evident from Figures 9.08-9.10 that removal of Cu from solution increases with time and equilibrium is attained in 10-15 minutes for a range of the initial concentrations of Cu. The maximum removal of Cu from the solution phase was found to be 99% where the initial concentration was 10 ppm and 98% removal was achieved for the initial concentration of 50 ppm and amount adsorbed was 80% for the initial concentration of 100 ppm. The same patterns were achieved for Cd, Ni, Pb and Zn (Figures 9.11-9.16). The adsorption of Zn [Zn (10 ppm) 10 ml/g] increases from 82% to 93% and 65% to 70% when the initial concentration was 100 ppm in 15 minutes. The adsorption of lead increased from 97% to 99% where the initial concentration was 100 ppm in 10 minutes, increase in Cd and Ni adsorption is recorded to be 91% to 94% and 72% to 80% in 15-minute time interval.

All these results indicate that adsorption of heavy metals onto soils is a

Table 7. Relative Adsoption Density of Heavy
Metals Adsorbing onto Soils [(10 ppm) 10 ml/g]

Metal	Adsorption Density Γ (μg/g)
Lead	100
Copper	99
Zinc	93
Cadmium	94
Nickel	80

rapid process and a major fraction of total metal load is removed from the aquatic phase in 15-20 minutes, for a wide range of initial concentration of adsorbate (10 ppm to 100 ppm). The data indicates that lead adsorbs more strongly than coppper, cadmium, zinc and nickel and the relative affinity of soils for various heavy metals increases in the following order:

Pb > Cu > Cd > Zn > Ni 9.4

and the adsorption density (Γ, total amount of adsorbate adsorbed per unit weight of adsorbent) is shown in Table 7 [from separate static adsorption systems with initial concentration of (10 ppm) 10 ml/g], which shows that adsorption density of various metals increases in the following order:

Pb > Cu > Cd > Zn > Ni

All these results show that adsorption of heavy metals onto soils is a rapid mechanism and the equilibrium is attained in 15-20 minutes for a wide range of concentrations of heavy metals and it was also noted that during the first two minutes of contact time a higher proportion of total metal concentration in the aqueous phase was adsorbed (Table 8).

Table 8. Adsorption of Cd, Cu, Ni, Pb and Zn onto soils
(percent adsorbed in 2-minute contact time)

Metal	Initial concentration (ppm)	Percent adsorbed in 2 min. contact time
Cadmium	10	91.5
Copper	10 100	95 70
Nickel	10	72
Lead	10 100	98.5 98
Zinc	10 100	87 66

9.4 Adsorption of Metals onto Soils From Sea-Water

Figures 9.09, 9.10 and 9.17, 9.18 show the adsorption behaviour of Cu from fresh and sea-water respectively onto soils under the identical conditions. Figure 9.09 shows that after 10 minutes contact of the Cu test solution into the system, 98% of the total amount of Cu was removed from the solution phase while Figure 9.17 shows the adsorption behaviour of Cu in sea-water and the amount adsorbed, in this case, was 93% of the total metal in the system. The similar pattern is observed for lead and zinc (Figures 9.12 and 9.20 and 9.13 and 9.19).

All these results show that the relative adsorption capacity of soils for heavy metals decreases in sea-water in comparision with fresh water systems (Table 9). The affinity of soils for heavy metals is much more stronger than Na^+ (as these metal ions distinguish themselves from alkali and alkaline earth ions in solution by displaying multiple hydrolysis at pH values encountered in the environment) but the higher concentration of sodium and magnesium in the system suppress the adsorption of metals by decreasing the quantity of available binding sites and by making the electrostatic conditions at the solid/solution interface unfavourable for further cation adsorption.

The presence of additional anions such as carbonates and chlorides may also influence the adsorption of heavy metal ions by strongly interacting with

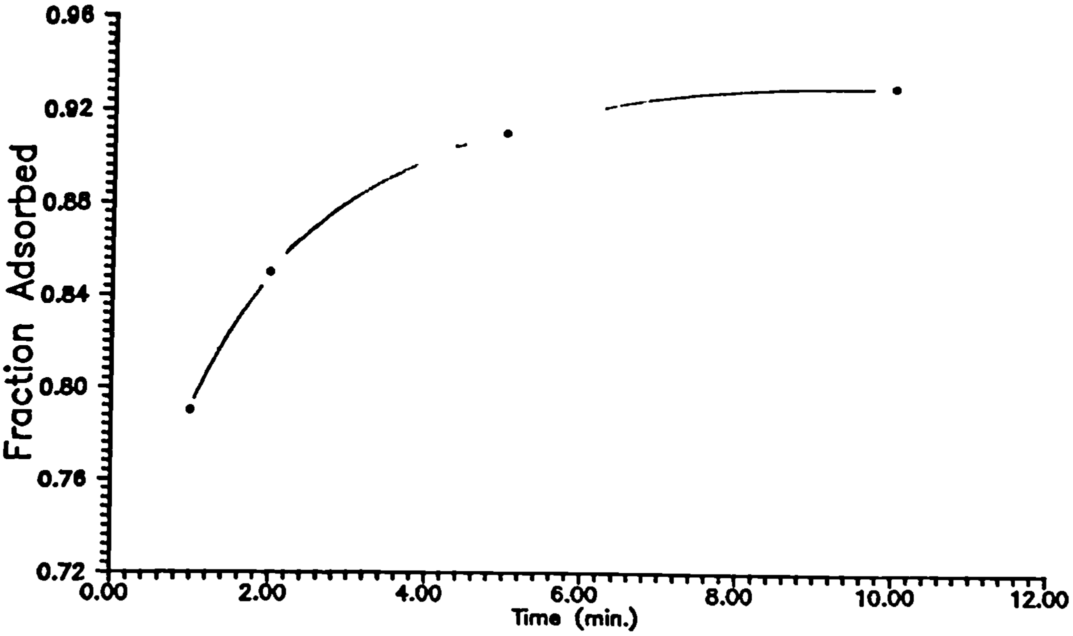


Figure 9.17

Adsorption of Cu onto soils as function of time

Cu(50 ppm)10 ml/g (sea-water)

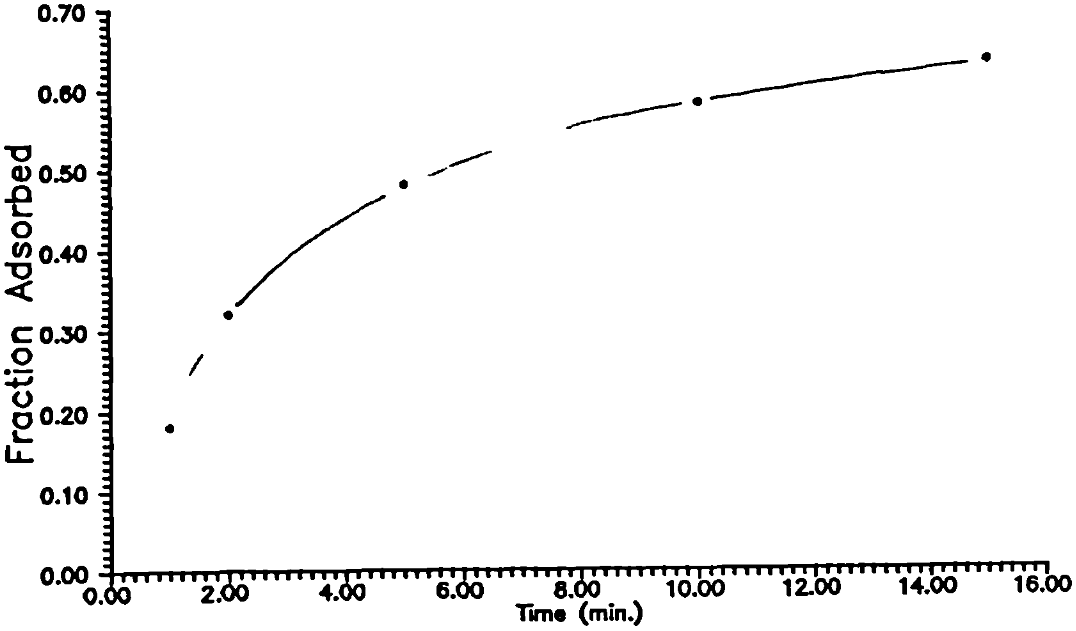


Figure 9.18
Adsorption of Cu onto soils as function of time
Cu(100 ppm)10 ml/g (sea-water)

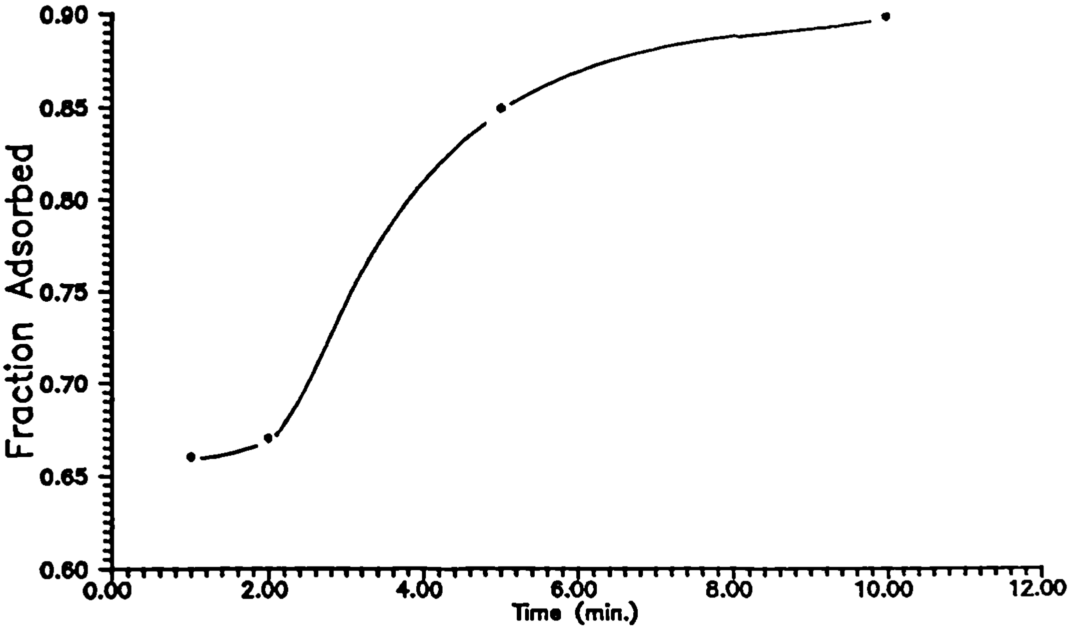


Figure 9.19
Adsorption of Pb onto soils as function of time
Pb(100 ppm)10 ml/g (sea-water)

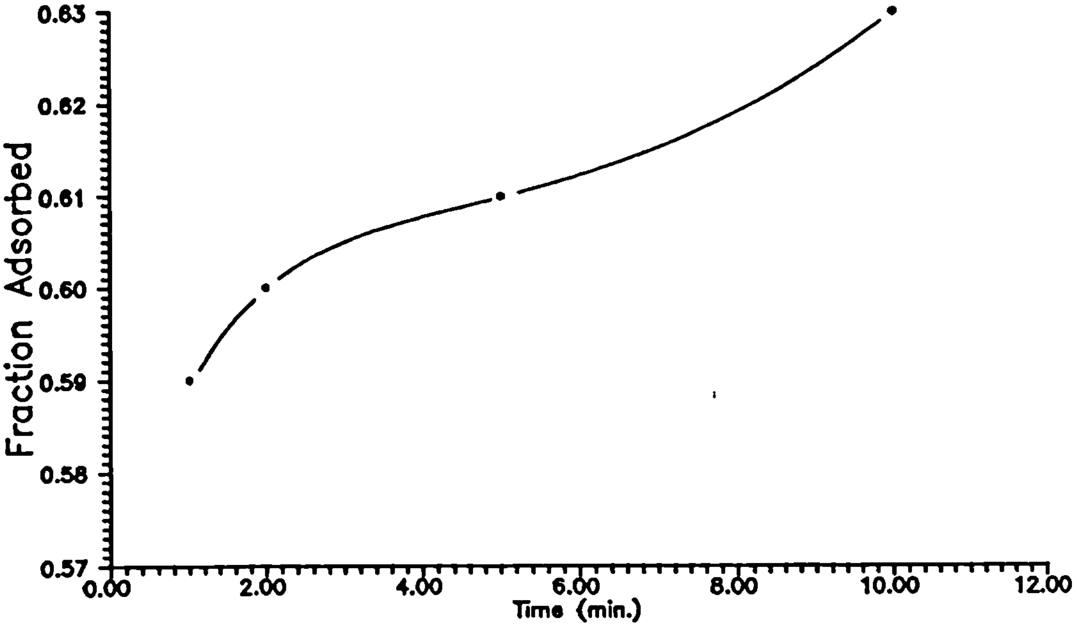


Figure 9.20
Adsorption of Zn onto soils as function of time
Zn(100 ppm)10 ml/g (sea-water)

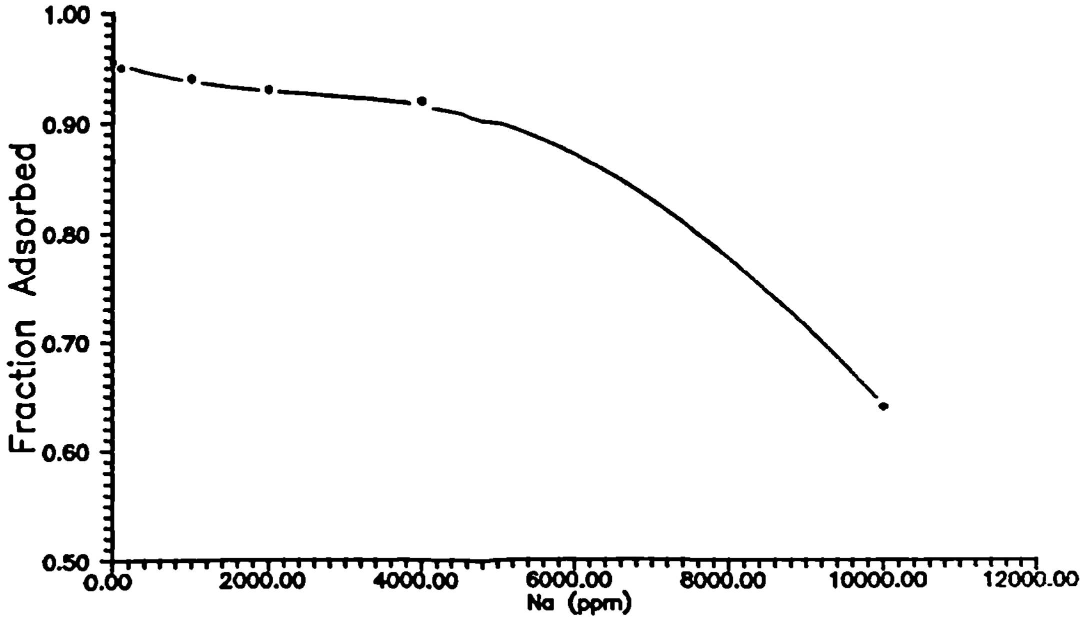


Figure 9. 21
Adsorption of Pb onto soils as function of Na^+ concentration
Pb(100 ppm)10 ml/g

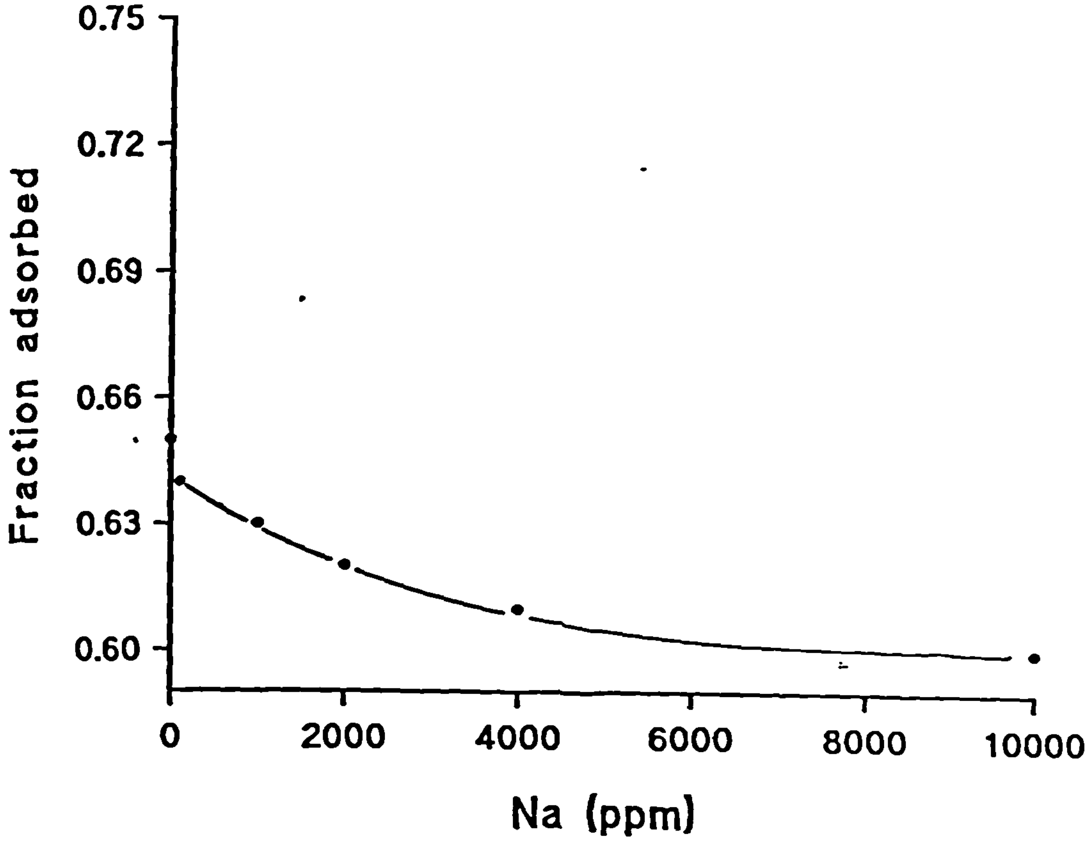


FIGURE 9.22
Adsorption of Zn onto soils as function of Na^+ concentration [(100 ppm)10 ml/g]

Table 9. Adsorption of Cu, Cd & Pb in freshwater and seawater
[(100 ppm) 10 ml/g]

Metal	Percent adsorbed in freshwater	Percent adsorbed in seawater
Pb	99	90
Cu	82	65
Zn	70	63

the clay minerals and, thereby, altering the electrostatic conditions at the interface or by forming solution complexes with the metals, so in marine environment, heavy metals are more persistent than in fresh-water system. In general, the major ions in an oxide-solution system are thought to control the electrical aspects of the interface, the trace ions are, therefore, susceptible to the electrostatic conditions imposed by the major ions. However, not only are the quantity and types of ions that are adsorbed important, but also the speciation of the adsorbed ions is also important. The binding of one ion can effect the double layer potential so as to increase, decrease or have no effect on the adsorption of other ion. The direction and extent of the effect, in part, depends on the charges of the adsorbed species.

A governing equation for adsorption introduced by Stumm & Morgan (1970) is given below:

$$\mathrm{Log}\frac{(M^{+Z})_{ads}}{(M^{+Z})_{diss}} = \frac{-ZF\sigma 4\Pi}{RT\xi\chi}$$

where

$(M^{+Z})_{ads}$ = the concentration of cations of valence Z in layer adjacent to the solid surface
$(M^{+Z})_{diss}$ = the concentration of cations in the bulk solution
F = Faraday constant
R = universal gas constant
T = absolute temperature
σ = charge density of solid surface (-ve for cations)
ξ = reciprocal distance of the thickness of the layer of adsorbed ions.
χ = dielectric constant of the medium

The term ξ increases with increasing Na^+ concentration. In fresh water the layer of cations is more diffuse and thick than in sea-water. To reach the surface the specifically adsorbed cation must diffuse from solution to the surface. This may be slower in sea-water because while the layer of electrostatically adsorbed cations is thinner it is, therefore, more concentrated and present a barrier to cation diffusion. Adsorption behavior of Zn and Pb is shown in Figures 9.21 and 9.22 as function of Na^+ concentration in the system. In both the cases, with increasing Na^+ in the system the amount adsorbed decreases. Although, Zn and Pb adsorb onto soils more strongly but very high concentration of Na^+ may cause desorption and/or low adsorption of metal ions as single site-types causes competition between heavy metals and Na^+.

The remobilization of heavy metals from suspended material and sediments is potentially hazardous not only for aquatic ecosystem but also for potable water supplies. At a constant pH there is a tendency toward desorption as salinity rises. So, remobilization is caused by a change in the salinity of water from fresh water to marine environment. When transported from river to estuary, the sediments are transported from the fresh water conditions, through fresh water to brackish water to marine water. In the process heavy metal compounds in the sediments will react to the change in the salinity, tending towards chemical equilibrium with the new environment. Downstream of the fresh water tidal area of the river a number of metals are mobilized to a lesser for greater extent, going into solution. Frenet (1981) placed Loire Estuary suspended matter into fresh and salt water (35 g/kg salinity) and studied the desorption of Hg, Cd and Pb, the results of which are shown in Table 10 which shows the role of salinity in the remobilization of metals in the aqueous environment. When the adsorption of metals onto solid surfaces in thesea-water or the desorption of adsorbed metal ions is studied, it shows that the adsorbed metal ions are presumably displaced by magnesium and sodium ions or these ions compete with metal ions for exchange sites in the system.

One of the most important examples of salt-water/sediment interactions can be found in the mixing zone river/sea i.e., estuarine environment. It is suggested that the distribution of heavy metals in particulate matter and in sediments is dominated by mixing processes between river-induced materials (more or less polluted) and sea-derived (fairly uncontaminated) particulates (Forstner & Muller,1974). In addition to this presumption one must suppose that still other processes are at work which may cause remobilization of heavy metals from particulates by desorption or by dissolution. The fate of heavy metals in estuaries is controlled by processes that take place at two interfaces (Windom, 1975): (a) Those occurring at the river-estuary boundary involving different salt concentrations, suspended material, pH values. (b) At the second interface, estuary-sediment boundary, metals are lost from the system because of precipitation and accumulation; and conversely, previously accumulated metals are released by chemical reaction and biological activity.

Table 10. Desorption of Hg, Cd & Pb in fresh and seawater mediums. (Frenet,1981)

Metal	Percent desorbed in freshwater	Percent desorbed in seawater
Hg	1.3	1.60
Cd	6.7	28.0
Pb	2.5	3.90

The processes chiefly influencing this distribution of dissolved metals are adsorption/ desorption, precipitation/ solubilization, flocculation, and complexation. There are, however, processes not only involving elevated salt concentrations but also, and often preferentially, those involving effects of oxidation and reduction, particularly of iron and manganese compounds, and reactions with organic matter (Goldberg,1975). Altogether, a very complex system of interactions exists that is still not completely understood, especially with respect to the behaviour of heavy metals.

9.5 Surface Loading

The extent of metal adsorption at any given point is also affected by surface loading i.e., the total metal concentration per unit mass of adsorbent, already present. Therefore, a comparison of the extent of metal adsorption can not be made without considering the surface loading. The percent of further metal adsorption increases with decreasing surface loading. The adsorption of Cu(II) onto soils as function of time is shown in Figure 9.08. The fraction adsorbed increases from 94% to $\overset{99}{98}$% in 15 minutes and the amount adsorbed increases from 94 µg/g to $\overset{99}{98}$ µg/g. Figure 9.09 shows the adsorption of Cu(II) from a solution with initial concentration of 50 ppm onto soils. The fraction adsorbed increases from 89% to 98% and the surface loading increases from 445 µg/g to 490 µg/g. Figure 9.10 shows the adsorption behaviour of Cu where the initial concentration is 100 ppm. It shows that the percent adsorbed increases from 68% to 80% i.e. from 686 µg/g to 800 µg/g respectively. The same pattern is observed for Cd, Ni, Pb and Zn (Figures 9.11-9.16). The relative adsorption capacity of soils, under the identical conditions, to adsorb heavy metals is shown in Table 11, which shows that these values increase in the following order:

Pb > Cu > Cd > Zn > Ni...... 9.5.

All these results show that as the amount of total metal is increased the fraction adsorbed decreases. In any system the adsorbent has limited

Table 11. Adsorption of Cd, Cu, Ni, Pb and Zn onto soils

Metal	Initial Conc.(ppm)	Adsorption Density, Γ (μg/g)
Lead	10	100
	20	198
	100	990
Copper	10	99
	50	496
	100	800
Zinc	10	93
	100	700
Cadmium	10	94
Nickle	10	80

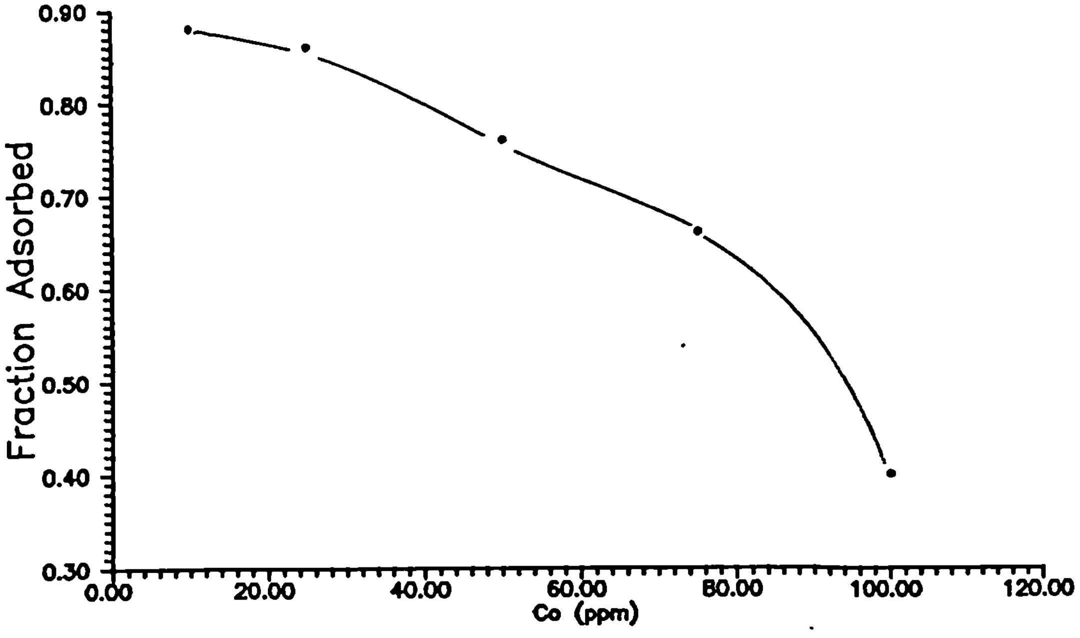


Figure 9.23
Adsorption of $Z\bar{n}$ onto soils as function of adsorbate **concentration**
(2g + 20 ml)

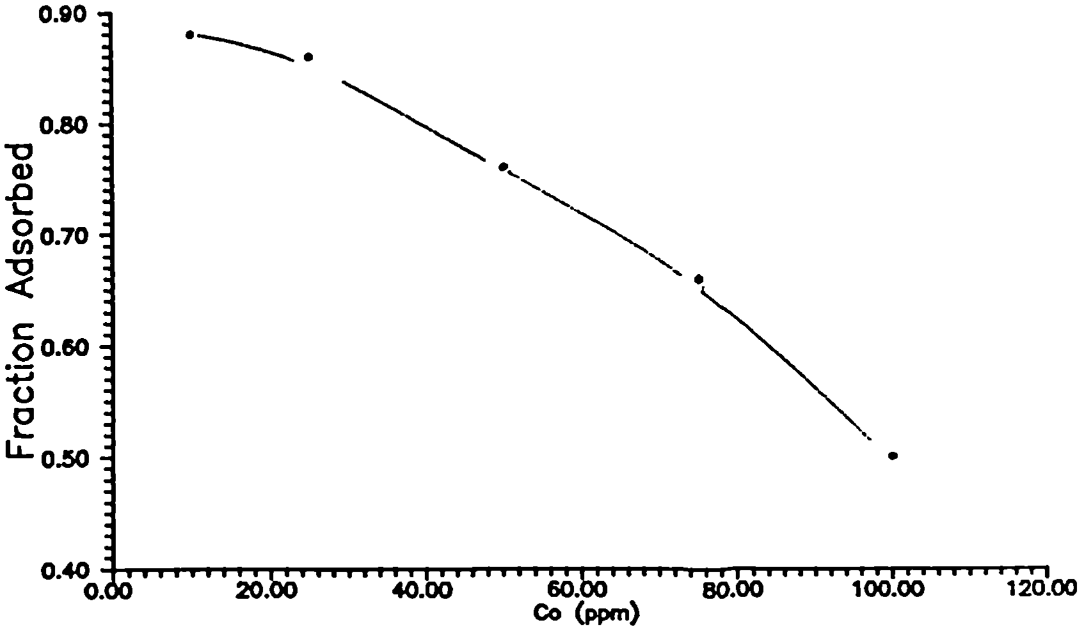


Figure 9.24
Adsorption of Cu onto soils as function of adsorbate **concentration**
(2g + 20 ml)

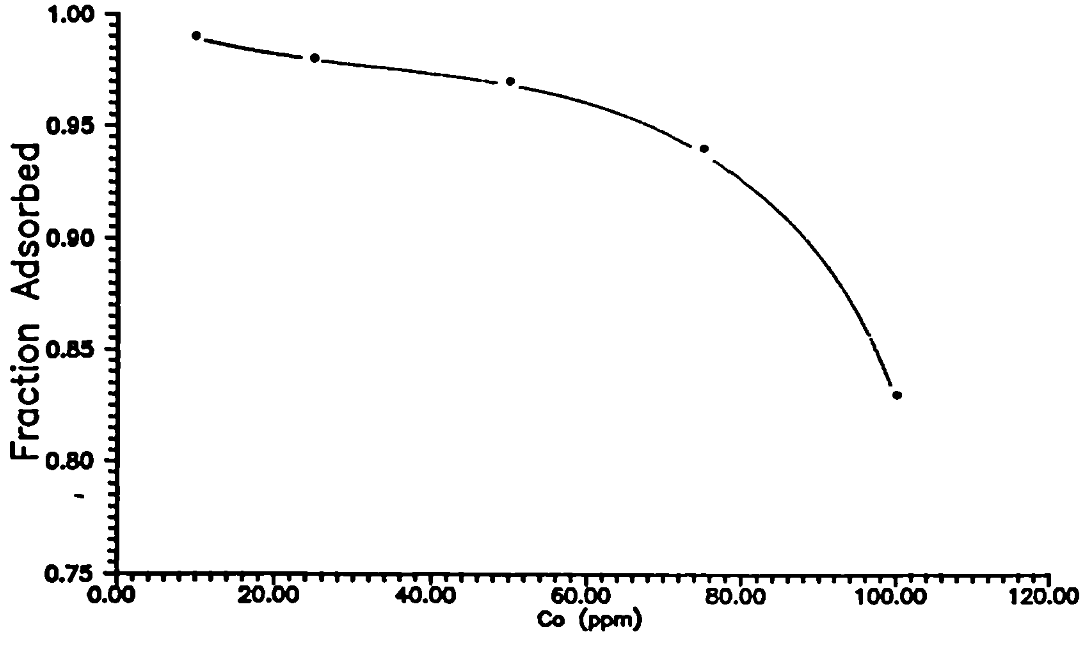


Figure 9.25
Adsorption of Pb onto soils as function of adsorbate concentration (2g + 20 ml)

adsorption sites available to the adsorptive. At lower concentrations of heavy metals there are enough sites to accommodate a large fraction of these metals but when the concentration of metals increases, a lower fraction of total metal concentration was adsorbed decreasing the fractional adsorption (Figures 9.23 - 9.25). Where, C is the initial concentration of metal in the system, the fraction adsorbed decreases with increasing the initial concentration of metal but the amount adsorbed increases from 88 μg/g to 600 μg/g for Zn, 88 μg/g to 500 μg/g for Cu and 100 μg/g to 833 μg/g for Pb (where the initial concentration of metal increases from 10 ppm to 100 ppm). Figures 9.26 and 9.27 show that with increasing amount of adsorbent in the system adsorption density, Γ (amount of adsorbate adsorbed per unit weight of adsorbent (where m(g) is mass in grams), decreases but the total amount of adsorbate adsorbed remains almost the same (Table 12 & Table 13).

Batch experiments (static adsorption system) were conducted to study the adsorption of Cu, Cd, Co, Ni, Pb and Zn onto soils from mixture containig [Cu, Cd, Co or Ni, Pb and Zn]. The adsorption behaviour of Cu , Cd , Ni , Pb and Zn is shown in Figures 9.08, 9.15, 9.16, 9.33 and 9.36 where the fraction adsorbed increased from 94% to $\overset{99}{98}$%, 91% to 94%, 72% to 79%, 97% to 99% and 87% to 95% for Cu, Cd, Ni, Pb and Zn respectively in 10-15 minutes. Figures 9.28 & 9.29, 9.30 & 9.31, 9.32, 9.33 & 9.35, and 9.37 & 9.38 show the adsorption behaviour of Cu, Cd, Ni, Pb and Zn from mixtures of metals [Cu, Cd, Cr, Ni, Pb and Zn] and [Cu, Cd, Cr, Co, Pb and Zn] where the fraction

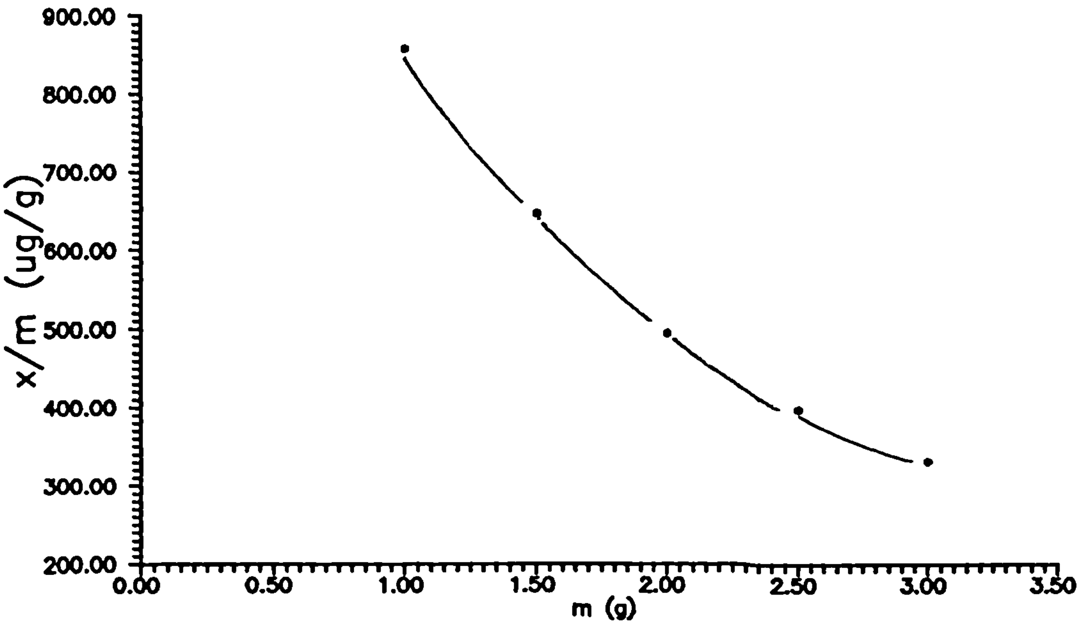


Figure 9.26.
Adsorption of Pb onto soils as function of amount of adsorbent (50 ppm + 20 ml)

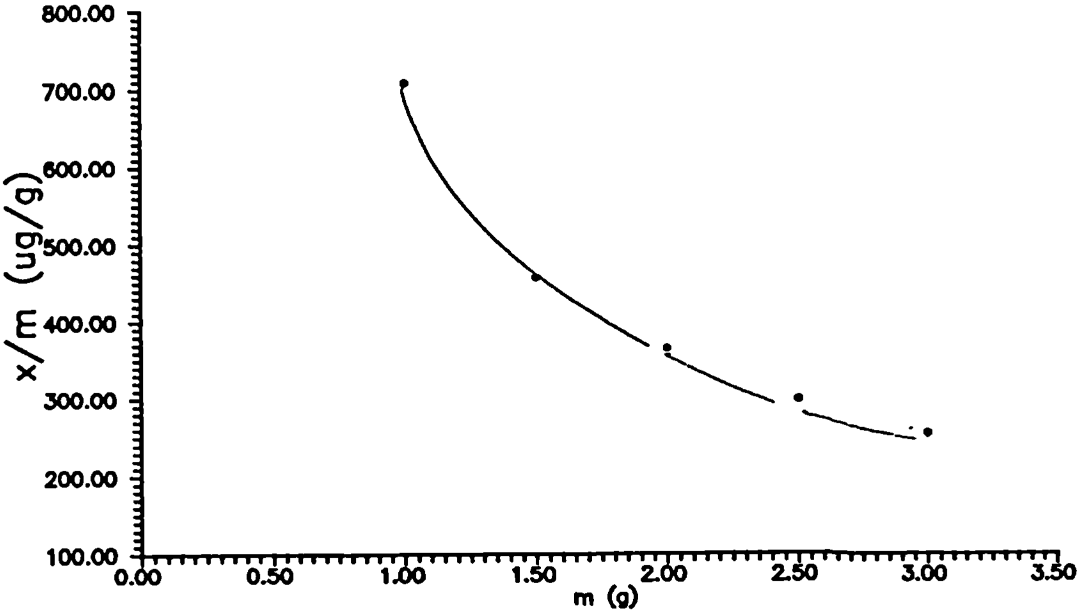


Figure 9.27
Adsorption of Zn onto soils as function of amount of adsorbent (50 ppm + 20 ml)

Table 12. Adsorption of Pb onto soils as function of amount of adsorbent (50 ppm + 20 ml)

Amount of adsorbate (g)	Adsorption density (µg/g)	Amount of adsorbate adsorbed (µg)
1	875	875
1.5	600	900
2	450	900
2.5	360	900
3	300	900

Table 13. Adsorption of Zn onto soils as function of amount of adsorbent (50 ppm + 20 ml)

Amount of adsorbate (g)	Adsorption density (µg/g)	Amount of adsorbate adsorbed (µg)
1	725	725
1.5	450	675
2	350	700
2.5	300	750
3	250	750

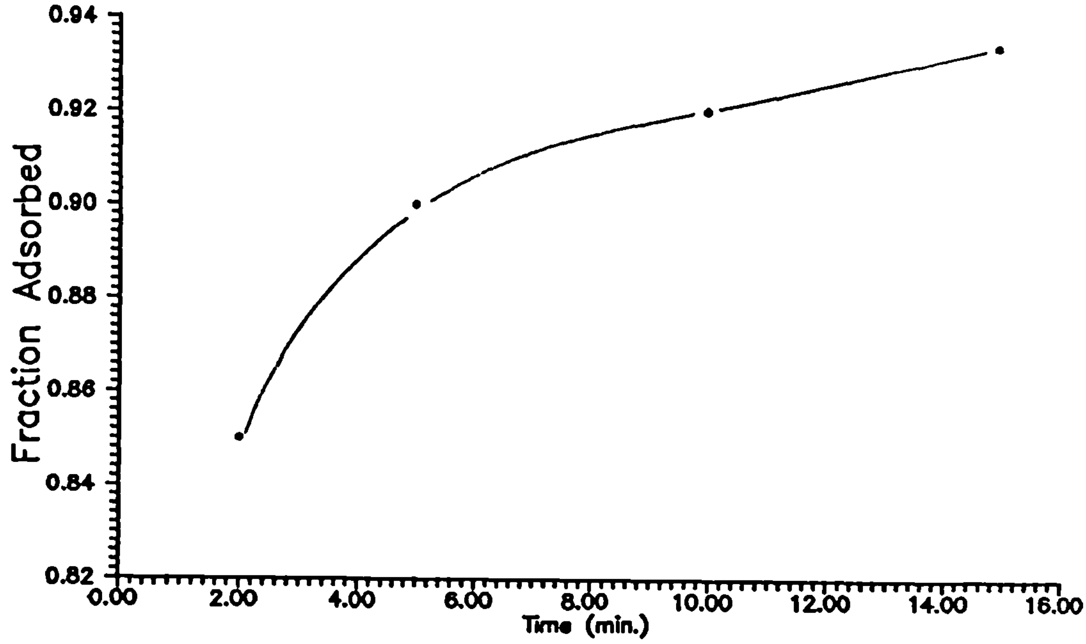


Figure 9.28
Adsorption of Cu onto soils as function of time
from mixture (Cd,Cu,Cr,Co,Pb and Zn) 10 ppm each
10 ml/g

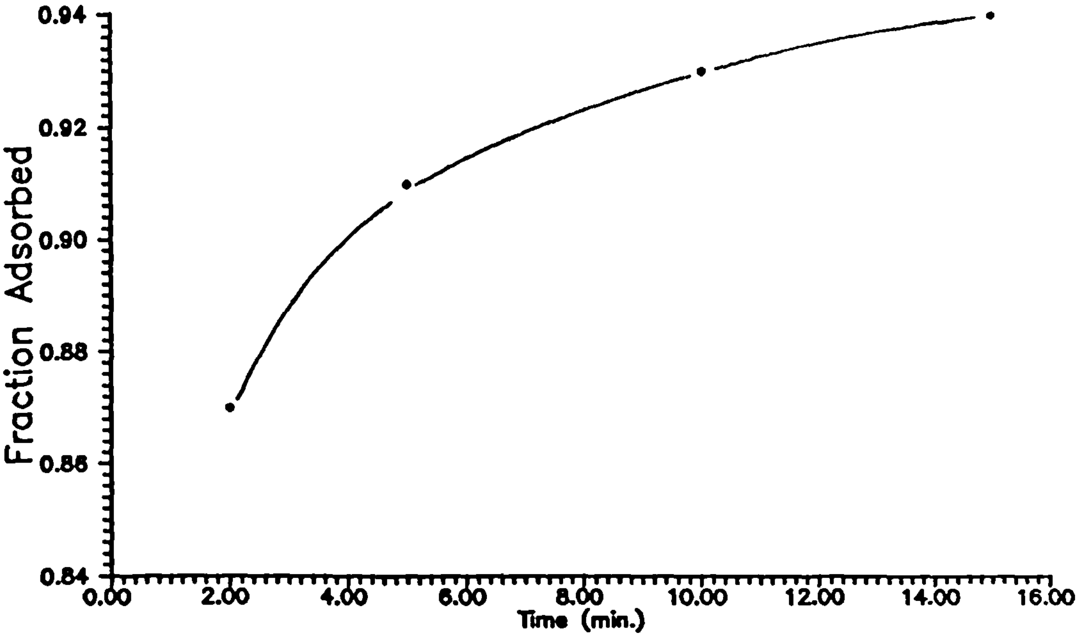


Figure 9.29
Adsorption of Cu onto soils as function of time
from mixture (Cd,Cu,Cr,Ni,Pb and Zn) 10 ppm each
10 ml/g

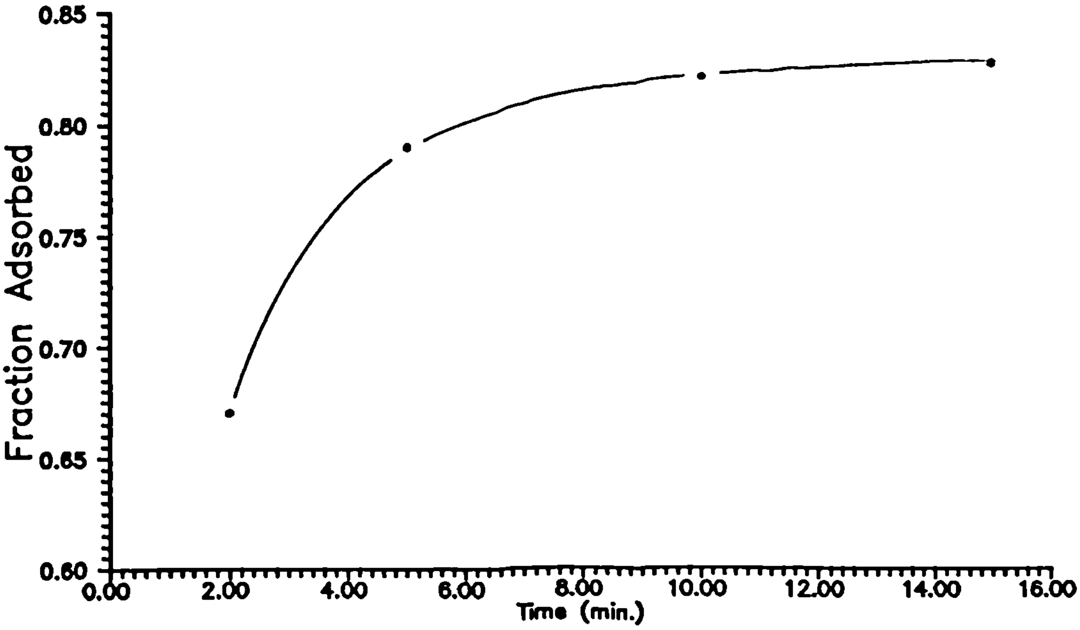


Figure 9.30
Adsorption of Cd onto soils as function of time
from mixture (Cd,Cu,Cr,Ni,Pb and Zn) 10 ppm each
10 ml/g

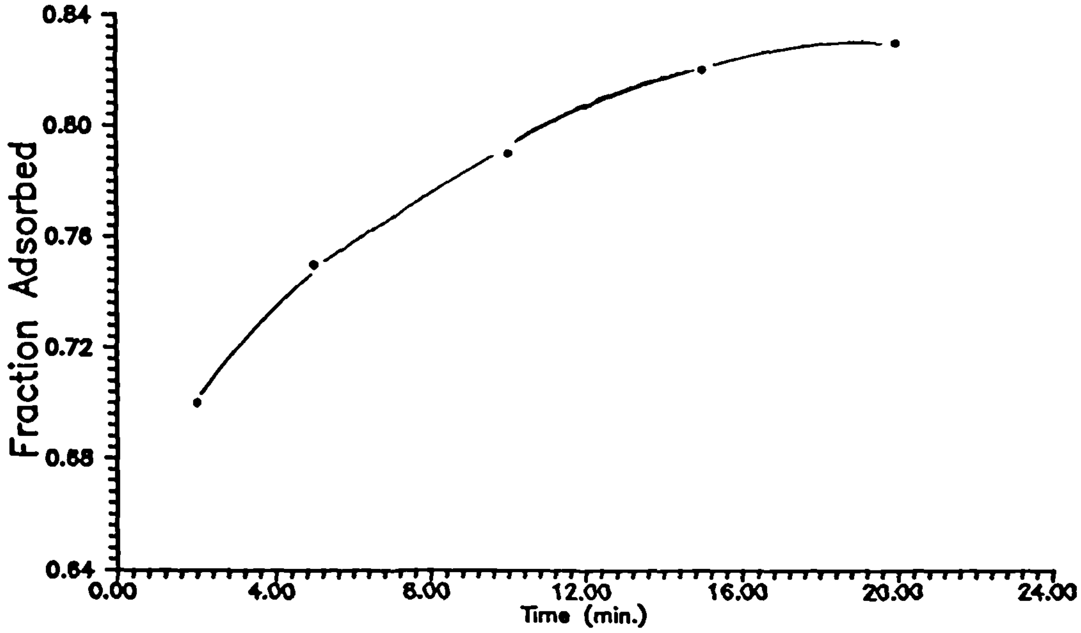


Figure 9.31
Adsorption of Cd onto soils as function of time from mixture
[Cd,Cu,Cr,Co,Pb and Zn (10 ppm each) 10 ml/g

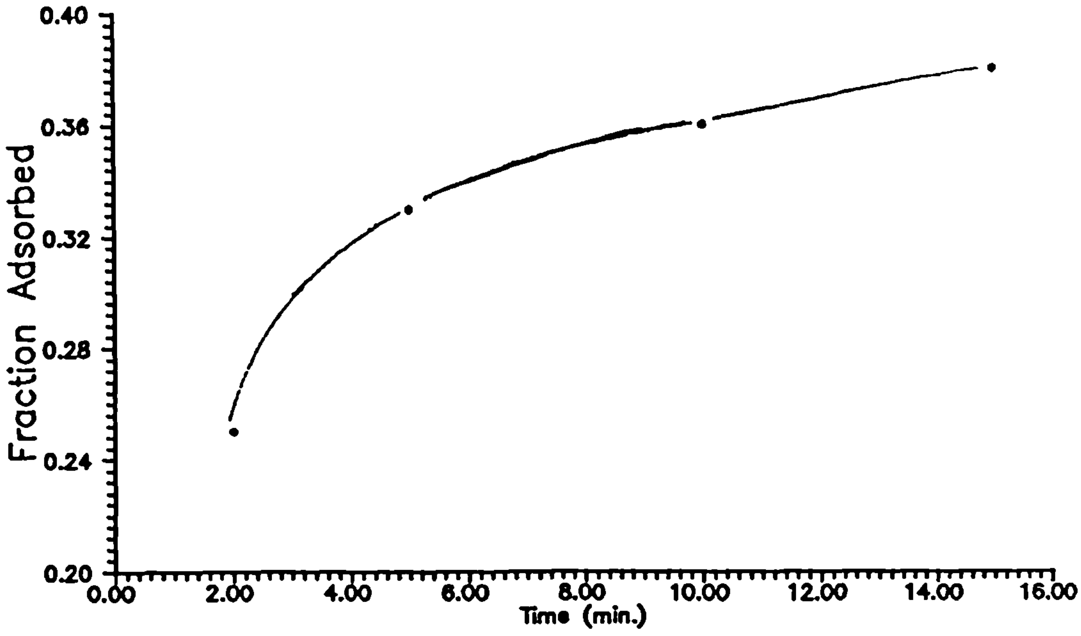


Figure 9.32
Adsorption of Ni onto soils as function of time
from mixture (Cd,Cu,Cr,Ni,Pb and Zn) 10 ppm each
10 ml/g

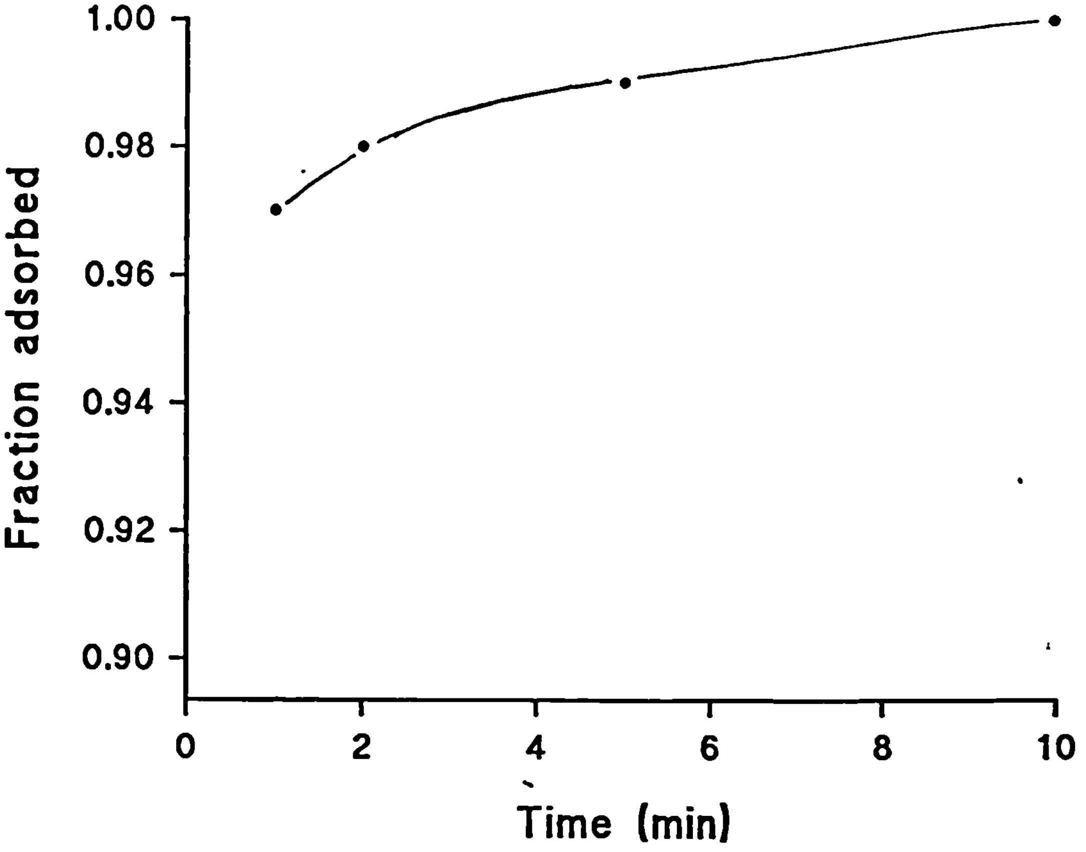


Figure 9.33
Adsorption of Pb onto soils as function of time
Pb(10 ppm)10 ml/g

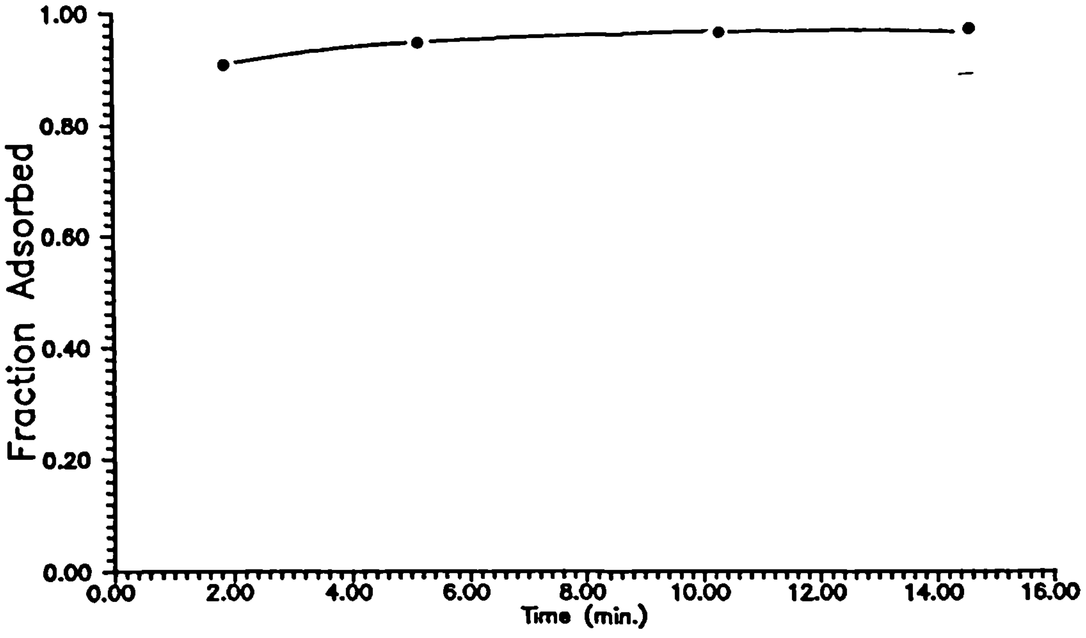


Figure 9.34
Adsorption of Pb onto soils as function of time
from mixture (Cd,Cu,Cr,Co,Pb and Zn) 10 ppm each
10 ml/g

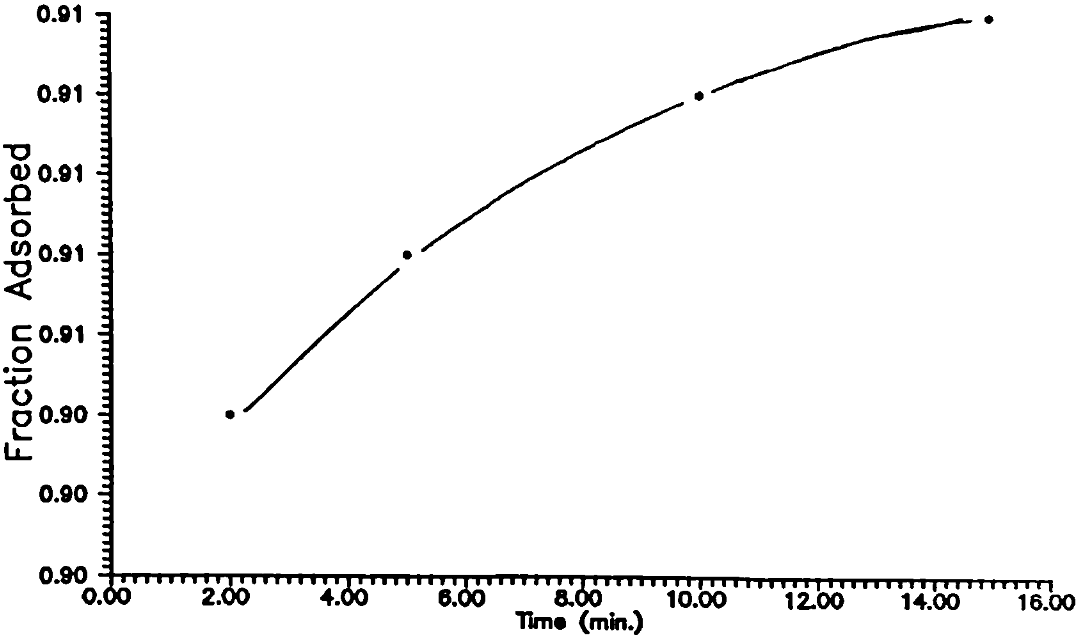


Figure 9.35
Adsorption of Pb onto soils as function of time
from mixture (Cd,Cu,Cr,Ni,Pb and Zn) 10 ppm each
10 ml/g

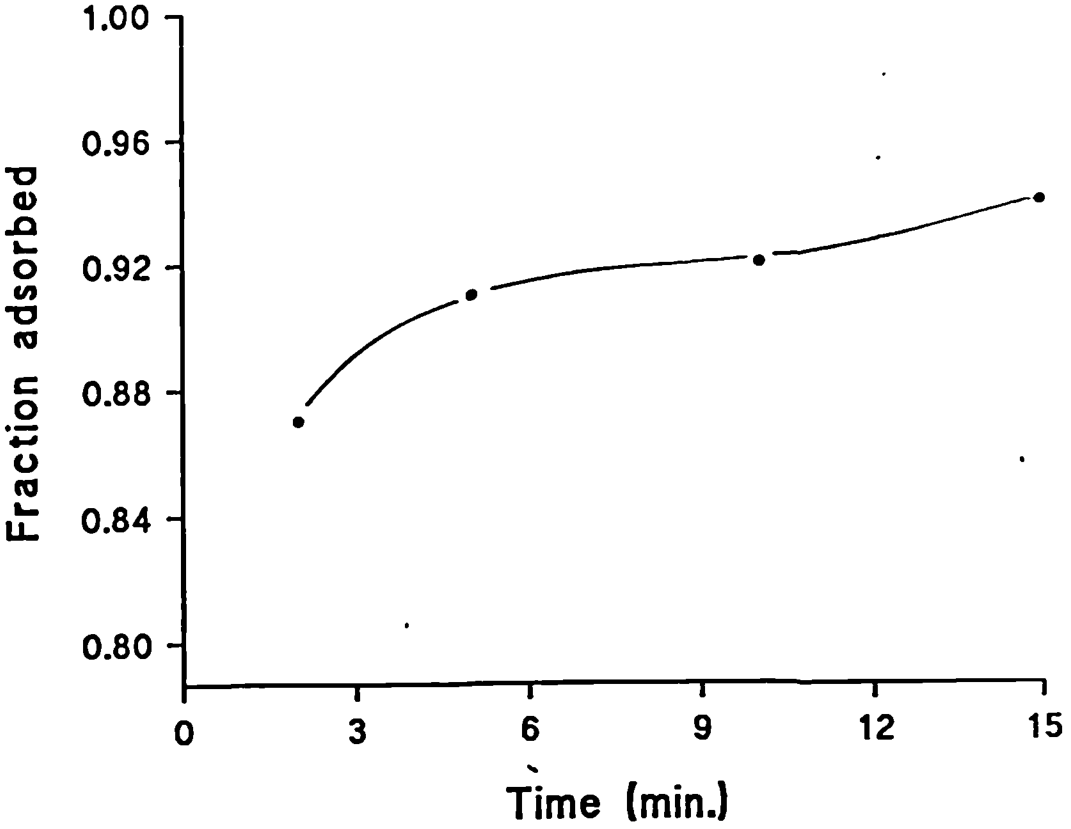


Figure 9.36
Adsorption of Zn onto soils as function of time
Zn (10 ppm) 10 ml/g

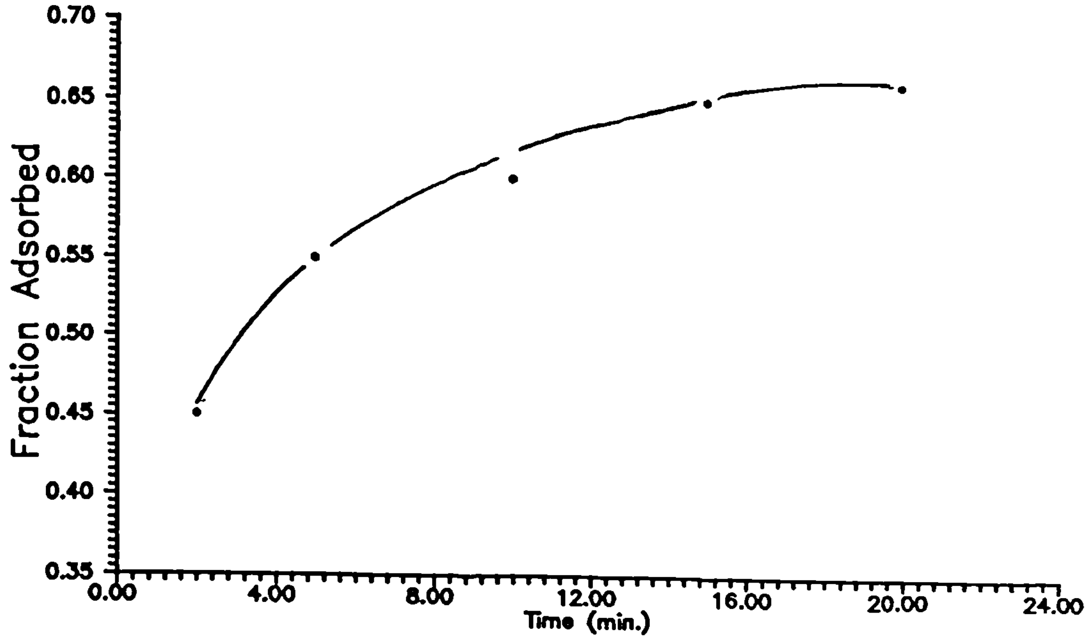


Figure 9.37
Adsorption of Zn onto soils as function of time
from mixture (Cd,Cu,Cr,Co,Pb and Zn) 10 ppm each
10 ml/g

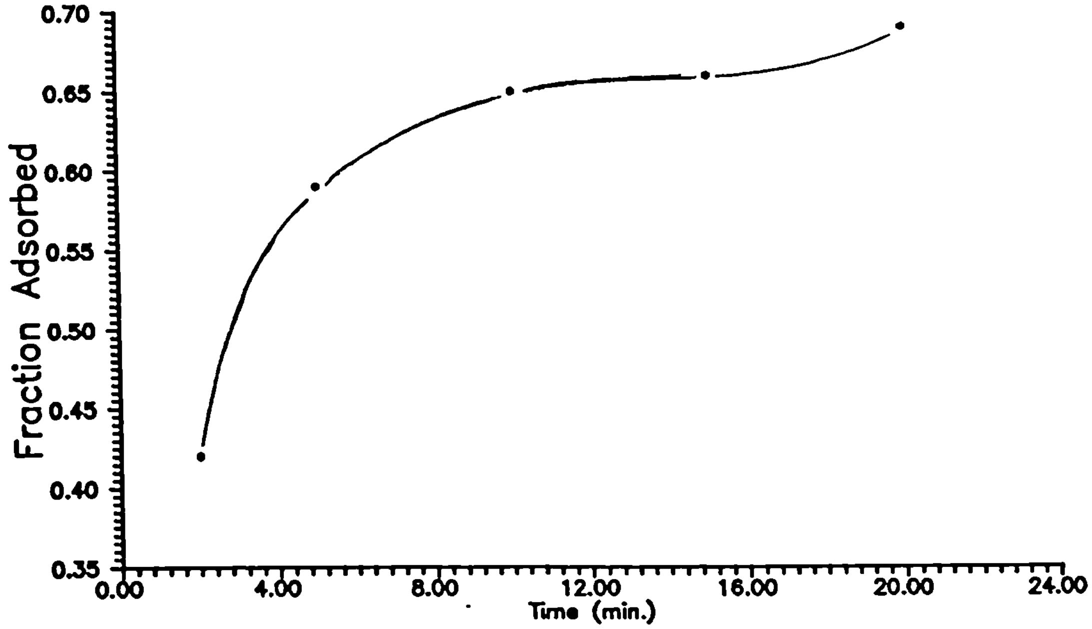


Figure 9.38
Adsorption of Zn onto soils as function of time
from mixture (Cd,Cu,Cr,Ni,Pb and Zn) 10 ppm each
10 ml/g

adsorbed decreased to 94%, 84%, 40%, 91% and 70% respectively.

All these results show the same pattern, i.e. the presence of one metal in the system effects the adsorption of another metal. The data show presence of Ni or Co in the mixture did not effect the adsorption behaviour of Cu, Cd and Zn very much but in the case of Pb the equilibrium was achieved in 5 minutes from the mixture containing cobalt. Although, the presence of another metal into the system generates the compitition for the exchange site, but the total amount of metal adsorbed is still less than the maximum adsorption capacitie (Table 3 & 14) so, the binding of one ion can effect the double layer potential so as to increase, decrease or have no effect on the adsorption behaviour of other ion.

1 g of soil was treated with H_2O_2 (to oxidize the organic contents of the sample) and the adsorption behaviour of Cu, Pb and Zn was studied (in static adsorption system). It is clear from Table 14 that amount of metal adsorbed onto soils either treated or untreated remains the same which clearly indicates that the clay minerals are the main adsorbing componennt and the organic contents of soil have no or a very little effect on the removal of metals from the system.

The adsorption behaviour of [Cu(100 ppm)10 ml/g] was studied onto soil, already loaded with Pb (990 μg/g). It was noted that the surface loading of Cu was 814 μg without replacing or desorbing Pb from the soils. Which shows that

Table 14. Adsorption of Cu, Pb & Zn onto soils [(100 ppm) 10 ml/g].

Metal	Percent Adsorbed (H_2O_2 treated sample)	Percent Adsorbed (Untreated samples)
Lead	98	99
Copper	83	82
Zinc	70	70

there is possibility of two or more surface site-types present for the adsorption of Cu and Pb. Table 3 shows the maximum adsorption capacities (Γ_{Max}) of various heavy metals onto soils and these values (Γ_{Max}) are quite higher than the surface loading of Pb which shows that there are still enough surface sites are available for Cu to adsorb without desorbing Pb from the solid. This argument is further strengthened when the adsorption behaviour of Cu [(100 ppm) 10 ml/g] was studied onto Pb saturated soils (by saturating the the sample [(1000 ppm) 20 ml/2g] in the metal test solution for 24h), the desorption of Pb was observed as Cu was adsorbed. These results prove that there is single site-type present and there is a compitetion between metal ion for surface sites. The maximum metal removal from the concentrated aqueous phase (10000 ppm) by adsorption onto soils is shown in Table 14. This shows quite high values with compare to data presented in Table 3, which shows the adsorption maxima for various heavy metals adsorption onto soils. Table 14 shows cation exchange capacity of soils, which is not necessarily the reflection of adsorption maxima. The data in Table 14 indicates the sum of exchangeable cation, cation exchange capacity, soils can exchange for various metals from the concentrated aquatic phase. The relative adsorption density (Γ) increases in the following order:

$$Zn < Cu < Pb$$

When trace metals enter into any aquatic system they are rapidly removed by various components of the ecosystem. Some of these metals may

Table 14. The maximum removal of Cu,Pb and Zn from the aqueous phase onto soils [(10,000 ppm)20 ml/2g]

Metal	Amount adsorbed (mg/g)
Copper	4.6
Lead	9.2
Zinc	4.2

be adsorbed on the surfaces of the available solids while a part of it may stay as free metal ions in the aqueous phase. The low concentration of metals in river or lake waters, despite the higher input rates, proves that there is a limited capacity of these available solids to adsorb metals and other contaminants on to their surfaces. At the first stage of their entrance, heavy metals are totally removed from the solution phase, in the meantime, as the new load arrives, a high fraction of total contaminant is removed until there comes a saturation point then total metal load stays into aqueous phase, diluted and dispersed. This could also explain the reasons that why the incident of Minamata disease occurred in 1964-65 although the plants of chemical firm Chisso Co. was established some years before and it was discharging methyl-mercury into the drainage channel which leads in to the bay.

9.6 The Selective Affinity of Soils For Heavy Metals (Dynamic Adsorption System)

The adsorption behavior of Cu and Zn from a mixture onto soils is shown (Figure 9.39) by using dynamic adsorption system. In the beginning of the process there were sites available in excess and adsorption of both Cu and Zn was taking place at low surface densities but as it proceeded the competition became stronger. Since the ionization potential of Cu and Zn are quite similar (Cu:2.71, Zn:2.70 eV.) the different adsorption behavior of these two metals can be attributed to the polarization effect. Cu^{+2} posses an unpaired electron in the 3d-orbital and is therefore more strongly polarized than Zn^{+2} (with no unpaired 3d electrons) and exhibits a greater affinity to anionic sites.

The adsorption behavior of Cu, Cd, Cr, Pb & Zn, Cd, Cr, Cu, Ni, Pb & Zn and Cd, Co, Cu, Pb & Zn from mixtures (in dynamic adsorption system) onto soils is shown (Figures 9.40, 9.41 and 9.42). It shows that the affinity of soils toward the heavy metals is in the following orders;

$$\mathrm{Zn} < \mathrm{Cd} < \mathrm{Cu} < \mathrm{Cr} < \mathrm{Pb}$$

$$\mathrm{Ni} < \mathrm{Zn} < \mathrm{Cd} < \mathrm{Cu} < \mathrm{Cr} < \mathrm{Pb}$$

$$\mathrm{Co} < \mathrm{Zn} < \mathrm{Cd} < \mathrm{Cu} < \mathrm{Cr} < \mathrm{Pb}$$

The Log values of the first hydrolysis product stability constant of various heavy metals are taken from Leckie and James (1974) and it shows that these

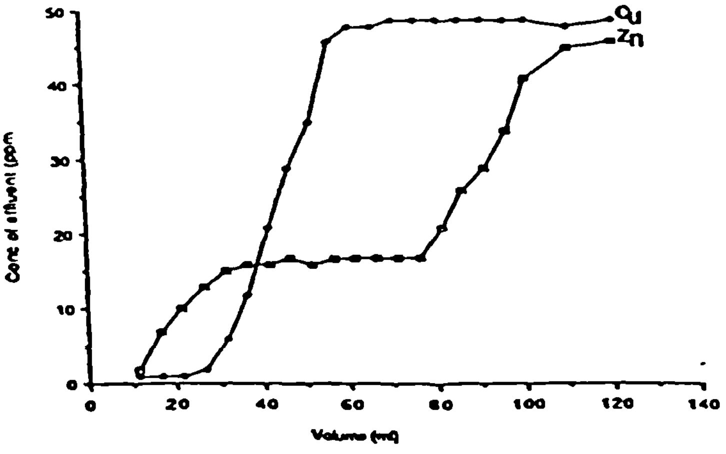


Figure 9.39
The breakthrough curves for Cu and Zn from mixture
(50 ppm each)
(Dynamic adsorption system)

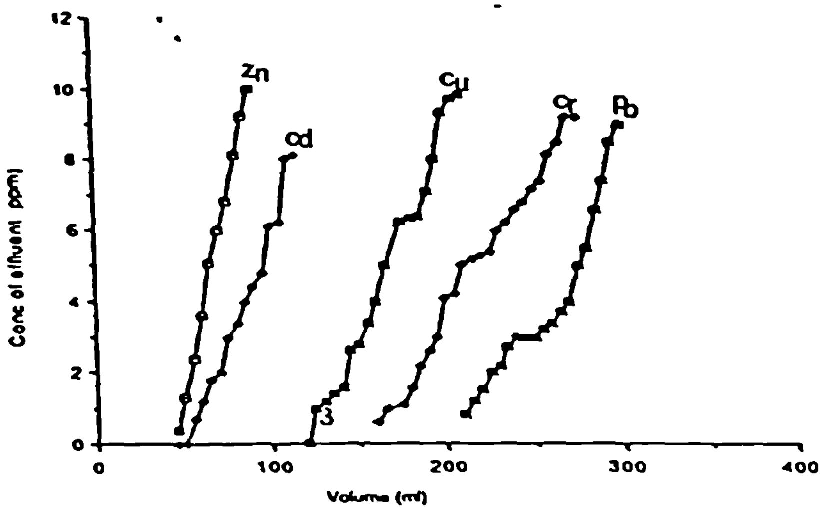


Figure 9.40
The breakthrough curves for Cd,Cu,Cr,Pb and Zn from mixture (10 ppm each)
(Dynamic adsorption system)

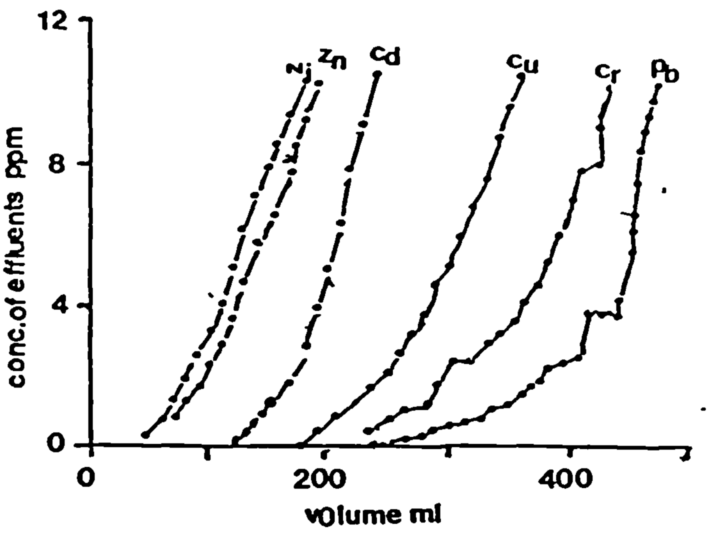


Figure 9 41
The breakthrough curves for Cd,Cu,Cr,Ni,Pb and Zn from mixture (10 ppm each)
(Dynamic adsorption system)

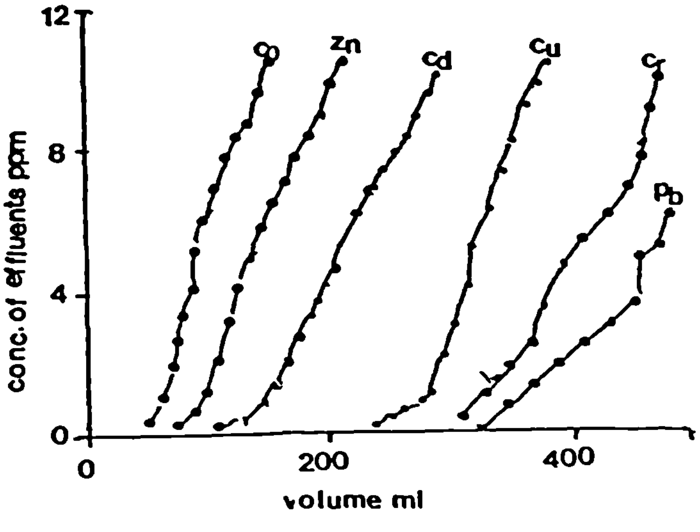


Figure 9 42
The breakthrough curves for Cd,Cu,Cr,Co,Pb and Zn from mixture (10 ppm each)
(Dynamic adsorption system)

values increase in the following order:

Co(II) < Zn(II) < Ni(II) < Cd(II) < Cu(II) < Cr(II) < Pb(II)

This may, again, indicate that the adsorption of heavy metals onto oxide surfaces / soils is a direct or indirect result of hydrolysis and further that the hydrolyzed metal ion species [$M(OH)^+$] is the adsorbing species. So if these values for any metal are known then its adsorption behaviour upto a certain limit can be predicted.

It is evident from Figures 9.40, 9.41 and 9.42 that total amount of various metals adsorbed, after passing 300 ml, 450 ml and 450 ml of test solution from the adsorption column, increases in the following orders:

Zn < Cd < Cu < Cr < Pb

Ni < Zn < Cd < Cu < Cr < Pb

Co < Zn < Cd < Cu < Cr < Pb

These results are in agreement with the other findings (relations 9.1, 9.4 & 9.5) showing the ralative adsoption capacity of soils for various metals increases in the same orders. These series are consistant with the the log values of metal hydroxy species equilibrium constants.

An apparent increase in cation exchange capacity may result from increased hydrolysis of the exchanging cations, since the hydroxy complexes i.e. $Cu(OH)^+$, are sorbed by most solids in preference to the uncomplexed cations, for example Cu^{2+} (James and Healy, 1972).

The affinity of the cations towards soils is governed by many factors which include valence and hydration effect, the affinity increases with increasing oxidation number(valence effect)

$M^+ < M^{2+} < M^{3+}$ ....

and with a decrease in the diameter of the hydrated cations, thus producing higher charge densities (Grim, 1968).

As the concentration of a solution increases, the number of exchanged cations likewise increases; exchanger in equilibrium with cations of different valence show preference for species with higher charge densities, an effect which becomes more pronounced upon dilution (increased valence effect).

As yet it is impossible to estabilish an order of affinities generally applicable to the individual heavy metals based solely on ionic charge and radius. Other factors, such as the tendency to form hydroxyl species or the tendency to adopt a particular geometric relation to the crystal latice of the exchanger, also play a significant role. Basic information about the atomic structure and oxidation states of Cd, Cu, Pb and Zn is provided in Table 15. For all the metals, the common oxidation state in aqueous solution is + II .

. Table 15. Basic chemical characteristics of Cd, Cu, Pb and Zn.

Metal	Atomic number	Atomic weight	Ionic radius (unhydrated)	Hydrated ionic radius
Cadmium	48	112.4	0.97 °A	5 °A
Copper	29	63.5	0.69 °A	6 °A
Lead	82	207.2	1.20 °A	5 °A
Zinc	30	65.4	0.74 °A	6 °A

Very little is known about the specific interactions of a wide range of ionic complexes that may occur in natural aquatic systems. In river systems different hydroxo- , carbonato- and aquo-inorganic metal complexes may occur. The adsorption of complexed ions by anionic sites is often more stable than the affinity for less hydrated cations (Forstner & Wittmann,1983). The observations of Block & Schindler (1970) on the sorption of radionuclides by River Rhine suspended materials show that significant uptake of heavy metals onto clay minerals within water does not occur. This is possibly due to other processes which, prior to clay adsorption, reduce the heavy metal contents in solution. On the other hand Jenne (1976) proposed that the most significant role of clay-size minerals in trace metal sorption by soils and sediment is that of mechanical substrate for the precipitation and flocculation of organic and secondary materials. Among the latter group of substances hydrous iron and manganese oxides have shown particularly strong affinities for trace elements. These affinities may involve mechanisms of adsorption and co-precipitation.

CONCLUSIONS

Based on this work, the following major conclusions are drawn:

1) The adsorption edges for Pb(II), Cu(II), Zn(II) and Cd(II) are in the range of 3.5-5.5, 3-6.5, 5.5-7.5, and 6-8 respectively.

2) The location of the adsorption region on pH scale is characteristic of a particular metal ion.

3) The $M(OH)^+$ species plays an important role in metal ion adsorption and it is likely that $M(OH)^+$ is predomonant metal surface species.

4) At lower pH values there is an increase in metal solubility and a decrease in metal retention, while at higher pH values metal retention increases because of lower solubility of metal species.

5) For most metal extraction with nitric and hydrochloric acid mixture (1:1) was not very effective while (1:2) and (1:3) gave the higher results. It was also observed that the extraction of metals from soils with the acid mixture of nitric and sulphuric acid was not very effective and the lowest results were recorded.

6) The adsorption of heavy metals onto soils is a very rapid process and a major fraction of the total metal concentration is removed from the aqueous phase in 15-20 minutes for a wide range of initial concentration of adsorbate.

7) It was noted that during the first two minutes of contact time a higher proportion of total metal concentration in the aqueous phase was adsorbed.

8) The fractional adsorption decreases with increasing the total metal concentration in the system.

9) The extent of metal adsorption at any given point is also affected by surface loading i.e., the total metal concentration per unit mass of adsorbent, already present. Therefore, a comparison of the extent of metal adsorption can not be made without considering the surface loading. The percent of further metal adsorption increases with decreasing surface loading.

10) The relative affinity of soils for various heavy metals increases in the following order;

$$\mathrm{Ni} < \mathrm{Zn} < \mathrm{Cd} < \mathrm{Cu} < \mathrm{Cr} < \mathrm{Pb}$$

11) The relative adsorption capacity of soils for various heavy metals increases in the following order:

Co-Ni < Zn < Cd < Cu < Cr < Pb

12) The relative adsorption capacity for heavy metals decreases in sea-water than in comparison with fresh-water systems and the higher concentrations of Na^+ in the system decreases the amount of heavy metals adsorbed onto soils.

13) At a constant pH there is a tendency toward desorption as salinity rises.

14) The binding of one ion can effect the double layer potential so as to increase, decrease or have no effect on the adsorption of other ion.

15) The main component of the soil, responsible for metal removal from the solution phase, was clay minerals.

16) There is single site-type present and all metal species compete for exchange sites into the soils.

17) The experimental data for adsorption of metal ions onto soils are described by the Langmuir adsorption isotherms and the adsorption

density of various metals increases in the following order:

Zn < Cu < Pb

FUTURE WORK

The need for future study in several areas has been realised during this research. Some suggested research topics are:

(1) Effect of natural organic matter on trace metal adsorption.

(2) Adsorption behaviour of natural organic matter and trace metal complexes with natural organic matter.

(3) Adsorption behaviour of trace metals adsorption with the presence of inorganic complexes

(4) From an engineering point of view, it would be valuable to study the distribution of surface site energies for several metals on various natural and model adsorbents. Such studies may establish some general patterns which could be used to predict metal partitioning in natural systems and engineering processes.

(5) To improve our capability to model reactions at oxide surfaces, there is a critical need to estabilish the causes for the variations among surface oxide sites. Research in this area should emphasise analysis of well characterized, pure solids both in the presence and absence of adsorbate.

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